Complete

PROCEEDINGS

OF

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Vol. XIII. Nos. 173–186.
JANUARY—DECEMBER, 1897.

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DATES OF ISSUE OF THE MONTHLY NUMBERS OF THE JOURNAL OF THE CHEMICAL SOCIETY TO FELLOWS.

January number was issued		22nd February.
February	„	23rd March.
March	„	8th April.
April	„	27th April.
May	„	13th May.
June	„	9th June.
July	„	19th July.
August	„	5th August.
September	„	1st September.
October	„	12th October.
November	„	5th November.
December	„	7th December.

LIST OF GRANTS MADE FROM THE RESEARCH FUND DURING THE YEAR.

£10 to Dr. J. J. Sudborough for the continuance of his researches on substituted cinnamic acids, and the stilbene series.

£10 to Dr. G. Young for the continuance of his researches on isomerism in the triazole series.

£25 to Mr. H. B. Baker for apparatus and materials for a research on tellurium.

£20 to Drs. J. J. Dobbie and Marsden for the purchase of corydaline for further investigations.

£10 to Dr. F. D. Chattaway for materials for the synthesis of orthodiphenylbenzene, and for a research on the action of sodium on the three dichlorobenzenes.

£10 to Prof. A. E. Dixon, M.D., for materials for an investigation of the action of thiocyanates on acid chlorides.

£10 to Dr. J. Walker for the preparation of normal acids of the succinic series.

£20 to Dr. J. J. Sudborough for the continuation of researches on diortho-substituted benzoic acids, unsaturated compounds, esters, &c.

£15 to Mr. W. J. Sell for a research on the chlorination of pyridine.

£10 to Mr. H. A. Auden for the preparation of a closed chain pentacarbon derivative from the ethylic ester of an acetoisocœnanthic acid.

£10 to Dr. F. E. Garrett for materials for an investigation of the pyridine bases of coal tar.

LIST OF FELLOWS ELECTED DURING 1897.

Name.	Proposed.	Elected.
Ackroyd, William	May 6th.	June 17th.
Alexander, John Owen	February 4th.	March 4th.
Aquino, Thomas Hannibal	January 21st	,, ,,
Arbuckle, William	,, ,,	,, ,,
Ashworth, John B.	February 4th	,, ,,
Ball, John, Ph.D.	June 3rd	December 2nd.
Ball, William	November 4th	,, ,,
Barclay, John, B.Sc.	February 4th	March 4th.
Barlow, Herbert W. L., M.A., M.B.	February 18th	May 6th.
Barlow, William	April 1st	,, ,,
Barlow, Walter Harry	May 20th	June 17th.
Bastow, Frank	February 4th	March 4th.
Beadle, Alec. Alfred	June 3rd	December 2nd.
Bhaduri, Jyoti Bhushan, M.A.	December 17th, 1896.	March 4th.
Boylan, Alfred Hunter	March 18th	May 6th.
Brierley, James	April 1st	,, ,,
Brothers, William Malam	May 6th	June 17th.
Brown, F. Hewlett Burton-, M.A.	February 18th	March 4th.
Brown, Gerald Noël	April 29th	June 17th.
Brown, James Herbert	December 3rd, 1896	March 4th.
Burland, Richard Oxley, J.P.	November 4th	December 2nd.
Cameron, Alexander McLean	,, ,,	,, ,,
Cameron, Ernest Stuart	May 20th	June 17th.
Cartmell, Alfred	December 17th, 1896.	March 4th.
Chikashigé, Masumi, B.Sc.	January 21st	,, ,,
Cholerton, Alfred Foster	,, ,,	,, ,,
Clarkson, Alexander	November 4th	December 2nd.
Clutterbuck, Medwin C., B.Sc., Ph.D.	May 20th	June 17th.
Collingridge, Frank, B.Sc.	November 4th	December 2nd.
Cranfield, William	May 6th	June 17th.
Creasey, Clarence Hamilton	January 21st	March 4th.
Crofts, James Murray, B.A.	November 4th	December 2nd.
Crowther, James, B.Sc.	January 21st	March 4th.
Daniell, John	November 4th	December 2nd.
Davidge, Henry Norris	March 18th	May 6th.
Davis, William Alfred	January 21st	March 4th.
Deverell, Louis Charles	February 18th	May 6th.
Diamond, William	December 17th, 1896.	March 4th.
Dixon, Andrew James	November 4th	December 2nd.
Dodgson, John Wallis, B.Sc.	December 3rd, 1896.	March 4th.
Duckham, Alexander	April 1st	May 6th.
Dufty, Lawrence	December 3rd, 1896.	March 4th.
Edwards, William Buckland	December 17th, 1896.	,, ,,
Fenby, Alaric Vincent C., B.Sc.	March 4th	May 6th.
Field, Charles Henry	,, 18th	,, ,,
Gibbons, Joseph Lake	December 3rd, 1896	March 4th.
Gilbody, Alexander W., M.Sc., Ph.D.	,, ,,	,, ,,

Name.	Proposed.	Elected.
Girtin, Thomas, B.A.	March 18th	May 6th.
Gomess, A. Bilderbeck	May 6th	June 17th.
Gough, Harold Walter, B.A.	December 3rd, 1896	March 4th.
Goulding, Ernest	January 21st	,, ,,
Grundey, Frederick Roscoe, B.Sc.	May 6th	June 17th.
Guest, Edward Graham, M.A.	February 4th	March 4th.
Guttman, Oscar	June 17th	December 2nd.
Guyer, R. Glode	March 4th	May 6th.
Halliwell, Edward	May 6th	June 17th.
Hamilton, Robert	November 4th	December 2nd.
Harbord, Frank William	May 20th	June 17th.
Harger, John, B.Sc., P.D.	November 4th	December 2nd.
Harley, Vaughan, M.D.	December 17th, 1896.	March 4th.
Harman, Harold	May 6th	June 17th.
Harris, Harold William	April 1st	May 6th.
Harrington, B. J., Ph.D.	May 20th	June 17th.
Hartley, Ernald G. Justinian, B.A.	December 3rd, 1896	March 4th.
Hartley, Thomas	February 4th	,, ,,
Heppenstall, Charles	January 21st	,, ,,
Hill, Sydney	April 1st	May 6th.
Holmes, John	February 4th	March 4th.
Horseman, James Walter	June 3rd	December 2nd.
Ibbotson, Fred, B.Sc.	December 17th, 1896.	March 4th.
Innes, William Rose, B.Sc., Ph.D.	November 19th, 1896	,, ,,
Jerdan, David Smiles, M.A., B.Sc.	December 17th, 1896.	,, ,,
Johnson, Harold	January 21st	,, ,,
Johnson, Otis C.	February 4th	,, ,,
Kelly, Charles	November 4th	December 2nd.
King, Herbert	February 4th	March 4th.
Lang, William Robert, B.Sc.	January 21st	,, ,,
Lasseter, W. J. G., M.A.	February 18th	May 6th.
Lee, Theophilus Henry	November 19th, 1896	March 4th.
Lemmey, Tom, B.A.	November 4th	December 2nd.
MacCulloch, Charles	March 18th	May 6th.
Mackenzie, John Edwin, B.Sc., Ph.D.	May 20th	June 17th.
Maclaurin, James Scott, D.Sc.	November 4th	December 2nd.
Macmullan, Alan, B.A.	,, ,,	,, ,,
Mallinson, Willie Lee	April 1st	May 6th.
Mansford, Charles Jodrell, B.A.	June 3rd	December 2nd.
Martin, Charles Henry	December 3rd, 1896	March 4th.
Masters, Edward	November 4th	December 2nd.
Matthews, John A., M.A., M.Sc.	,, ,,	,, ,,
Merson, George Fowlie	March 18th	May 6th.
Miller, Edmund Howd, M.A., Ph.D.	April 1st	,, ,,
Mitchell, Tom	March 4th	,, ,,
Moon, Philip George Gregory	November 4th	December 2nd.
Morgan, Frederick Filmer de	February 18th	May 6th.
North, Barker	January 21st	March 4th.
Orton, Joseph Previte K., B.A., Ph.D.	April 1st	May 6th.

Name.	Proposed.	Elected.
Parker, Charles Henry	February 4th	March 4th.
Philip, James Charles, B.Sc., Ph.D.	November 4th	December 2nd.
Phillips, Harry E.W., B.A.	February 18th	May 6th.
Pickard, Robert Howson, B.Sc.	March 4th	,, ,,
Pollitt, Samuel, B.Sc.	February 4th	March 4th.
Pollock, William Robertson	May 6th	June 17th.
Pullar, Herbert Spindler	January 21st	March 4th.
Ralston, William, B.Sc.	,, ,,	,, ,,
Reid, Alexander Ferguson	November 4th	December 2nd.
Remington, John Stewart	January 21st	March 4th.
Roberts, Ernest Henry	November 4th	December 2nd.
Rosling, Edward	December 17th, 1896.	March 4th.
Rutter, Alfred	January 21st	,, ,,
Scargill, Lionel Walter K., B.A.	May 20th	June 17th.
Shenton, James Porter	,, ,,	,, ,,
Simpson, Edward Sydney, B.E.	November 4th	December 2nd.
Smith, Robert Francis Wood	,, ,,	,, ,,
Southerden, Frank	November 19th, 1896	March 4th.
Southern, Thomas, junr.	June 3rd	December 2nd.
Stainer, William James, B.A.	December 3rd, 1896	March 4th.
Steel, Frederick William	November 4th	December 2nd.
Stephens, Michael Edmund	,, ,,	,, ,,
Stevens, Henry Potter, B.A.	December 17th, 1896.	March 4th.
Stubbs, George	November 4th	December 2nd.
Sumner, Leonard, B.Sc.	January 21st	March 4th.
Taverner, William	April 29th	June 17th.
Thompson, Harry	December 17th, 1896.	March 4th.
Tickle, Thomas	March 18th	May 6th.
Tripp, Edward Howard, Ph.D.	November 4th	December 2nd.
Turnbull, Andrew, Ph.D.	January 21st	March 4th.
Turner, Basil William	November 19th, 1896	,, ,,
Turner, John Scriven	November 4th	December 2nd.
Unwalla, Rustomji Navroji	January 21st	March 4th.
Viccajee, Framjee Khurshedjee	November 4th	December 2nd.
Vinter, Percy John, M.A.	,, ,,	,, ,,
Waite, William Herbert, B.A.	February 18th	May 6th.
Walford, Samuel Matthew	December 3rd, 1896.	March 4th.
Walker, J. Wallace, M.A., Ph.D.	,, ,,	,, ,,
Watts, Charles Thomas Foster	February 18th	May 6th.
Welsh, John	,, ,,	,, ,,
West, Charles Alfred	April 1st	,, ,,
While, Arthur James	November 4th	December 2nd.
White, Paul Thomas	April 1st	May 6th.
Wilderman, Meyer, Ph.D.	February 4th	March 4th.
Young, Francis Samuel, M.A.	June 3rd	December 2nd.

FELLOWS DECEASED.

Name.	Elected.	Died.
Bowrey, J. J.	December 16th, 1869	November 19th 1897.
Child, G. W.	January 16th, 1868	
Gaskell, E. H.	January 20th, 1876	November 18th, 1897.
Gibbins, B. H.	May 7th, 1891	May 8th, 1897.
Hammersley, W. A. L.	December 7th, 1882	December 26th, 1897.
Harris, S. J.	December 2nd, 1886	May 27th, 1897.
Jardine, Walter	February 18th, 1894	
Keyworth, G. A.	April 15th, 1875	May 27th, 1897.
Lackersteen, M. H.	February 3rd, 1859	December 7th, 1897.
Lees, Samuel	December 1st, 1887	April 17th, 1897.
Lescher, Herman	April 17th, 1890	March —, 1897.
Mitchell, Thomas	June 18th, 1891	September 9th, 1897.
Newton, Howard	December 18th, 1879	July 27th, 1897.
Rimmington, F. M.	December 4th, 1873	June 17th, 1897.
Rodger, J. W.	December 15th, 1892	May 30th, 1897.
Roy, Taraprasanna	June 17th, 1880	
Saint, W. J.	December 20th, 1883	May 11th, 1897.
Tomlinson, Charles	June 2nd, 1864	February 12th, 1897.
Wormley, T. G.	November 19th, 1885	January 3rd, 1897.

TITLES OF PAPERS COMMUNICATED TO THE SOCIETY DURING 1897.

	Page in Proceedings.	Page in Transactions.
January 21st.		
1. Observations on the properties of some highly purified substances. By W. A. Shenstone	2	471
2. The action of diastase on starch. By Arthur R. Ling and Julian L. Baker	3	508
3. The solution density and cupric-reducing power of dextrose, lævulose and invert-sugar. By Horace T. Brown, F.R.S., G. Harris Morris, Ph.D., and J. H. Millar	4	275
4. Derivatives of maclurin. Part II. By A. G. Perkin	5	186
5. Halogen-substituted acidic thiocarbimides and their derivatives; a contribution to the chemistry of the thiohydantoins. By Augustus Edward Dixon, M.D.	6	617
6. The amyl (secondary butyl-methyl) derivatives of glyceric, diacetylglyceric, and dibenzoylglyceric acids, active and inactive. By Percy Frankland, Ph.D., B.Sc., F.R.S., and Thomas Slater Price, B.Sc	9	253
7. The refraction constants of crystallised salts. By Alfred E. Tutton	10	235
8. The refraction constants of crystalline salts: A correction. By William Jackson Pope	11	—
9. On the wide dissemination of some of the rarer elements and the mode of their association in common ores and minerals. By W. N. Hartley, F.R.S., and Hugh Ramage	11	533
February 4th.		
10. Observations upon the oxidation of nitrogen gas. By Lord Rayleigh, F.R.S.	17	181
11. On some apparatus for steam distillation. By F. E. Matthews, Ph.D.	18	318
12. Researches in the Stilbene Series. I. By John J. Sudborough, Ph.D.	19	218
13. Diortho-substituted benzoic acids. III. Hydrolysis of substituted benzamides. By John J. Sudborough, Ph.D., Percy G. Jackson, and Lorenzo L. Lloyd	20	229
14. Conversion of camphoroxime into methylcamphorimine and camphenylnitramine. By M. O. Forster, Ph.D.	21	191
15. Note on Wechsler's method for the separation of fatty acids. By Arthur W. Crossley	21	580

	Page in Proceedings.	Page in Transactions.
16. On the crystalline structure of gold and platinum nuggets and gold ingots. By A. Liversidge, LL.D., F.R.S.	22	1125
17. On the presence of gold in natural saline deposits and marine plants. By A. Liversidge, LL.D., F.R.S.	22	298
February 18th.		
18. The formation of dithionic acid in the oxidation of sulphurous acid by potassium permanganate. By T. S. Dymond and F. Hughes.	42	314
19. On the production of pyridine derivatives from ethylic-β-amidocrotonate. By J. Norman Collie, Ph.D., F.R.S.	43	299
20. Sodamide and some of its substitution derivatives. By A. W. Titherley, M.Sc., Ph.D	45	460
21. Rubidamide. By A. W. Titherley, M.Sc., Ph.D.	46	469
22. On the spectrographic analysis of some commercial samples of metals, of chemical preparations, and of minerals from Stassfurt potash beds. By W. N. Hartley, F.R.S., and Hugh Ramage	46	547
23. Dissociation pressure of alkylammonium hydrosulphides. By James Walker, D.Sc., Ph.D., and John S. Lumsden, B.Sc., Ph.D.	48	428
24. Supposed condensation of benzil with ethyl alcohol. A correction. By Francis Robert Japp, F.R.S.	48	297
25. The viscosity of mixtures of miscible liquids. By T. E. Thorpe, F.R.S., and J. W. Rodger	49	360
26. Magnesium nitride as a reagent. By H. Lloyd Snape, D.Sc., Ph.D.	50	526
27. The identity of Laurent's amarone with tetraphenylazine. By H. Lloyd Snape, D.Sc., Ph.D., and Arthur Brooke, Ph.D.	51	528
28. Studies on the interaction of highly purified gases in presence of catalytic agents. Part I. By Wm. French, M.A.	52	—
29. Contributions to the knowledge of the β-ketonic acids. Part III. By S. Ruheman, Ph.D., M.A.	52	323
30. Contributions to the knowledge of the β-ketonic acids. Part IV. By S. Ruheman, Ph.D., M.A., and A. S. Hemmy, B.A., M.Sc.	53	329
31. Oxidation of phenylstyrenyloxytriazole. By George Young, Ph.D.	53	311
32. Apiin and apigenin. (Preliminary notice.) By A. G. Perkin	53	—
33. Note on the constitution of the so-called "nitrogen iodide." By J. W. Mallet, F.R.S.	55	—
March 4th.		
34. Some hydrocarbons from American petroleum. I. Normal and Iso-pentane. By Sydney Young, D.Sc., F.R.S., and G. L. Thomas, B.Sc.	58	440

	Page in Proceedings.	Page in Transactions.
35. The vapour pressures, specific volumes and critical constants of normal pentane; with a note on the critical point. By Sydney Young, D.Sc., F.R.S.	58	446
36. On the freezing-point curves of alloys containing zinc. By C. T. Heycock, F.R.S., and F. H. Neville	60	383
37. The oxides of cobalt and the cobaltites. By Arthur H. McConnell and Edgar S. Hanes	62	584
38. A new synthesis in the sugar group. By Henry J. Horstman Fenton, M.A.	63	375
39. The dinitrosamines of ethylene aniline, the ethylene toluidines, and their derivatives. By Francis E. Francis, Ph.D., B.Sc.	63	422
40. Contribution to the knowledge of the β-ketonic acids. Part V. By S. Ruhemann, M.A., Ph.D., and A. S. Hemmy, B.A., M.Sc.	64	334
41. Enantiomorphic forms of ethylpropylpiperidonium iodide. By Clare de Brereton Evans	64	522
42. Further note on ketopinic acid—pinophanic acid. By W. S. Gilles and F. F. Renwick	64	—
43. A synthesis of citric acid. By W. T. Lawrence, B.A., Ph.D.	65	457
March 18th.		
44. On the atomic weight of carbon. By Alexander Scott, M.A., D.Sc.	70	550
45. On a new series of mixed sulphates of the vitriol group. By Alexander Scott, M.A., D.Sc.	71	564
46. A synthesis of camphoronic acid. By William Henry Perkin, jun., F.R.S., and Jocelyn Field Thorpe, Ph.D.	72	1169
47. Note on a method for determining melting points. By Ernest H. Cook, D.Sc.	74	—
48. Velocity of urea formation in aqueous alcohol. By James Walker, D.Sc., and Sydney A. Kay, B.Sc.	75	489
49. Action of alkyl haloids on aldoximes and ketoximes. By Wyndham R. Dunstan, F.R.S., and Ernest Goulding	76	573
March 25th.		
Pasteur Memorial Lecture. By Professor P. Frankland, Ph.D., B.Sc., F.R.S.	79	683
March 31st.		
50. The hydrolysis of perthiocyanic acid. By F. D. Chattaway, M.A., and H. P. Stevens, B.A.	87	607
51. The composition of cooked fish. By Katherine I. Williams	88	649
52. On the oxidation products of αγ-dimethyl-α′-chloropyridine. By Emily Aston, B.Sc., and J. Norman Collie, Ph.D., F.R.S.	89	653

	Page in Proceedings.	Page in Transactions.
April 20th.		
53. On the explosion of chlorine peroxide with carbonic oxide. By H. B. Dixon, M.A., F.R.S., and E. J. Russell, B.Sc.	99	605
54. On the decomposition of iron pyrites. By W. A. Caldecott, B.A.	100	—
55. Monochlorodiparaconic acid and some condensations. By Henry C. Myers, Ph.D.	100	614
56. Corydaline. Part V By James J. Dobbie, M.A., D.Sc., and Fred Marsden, M.Sc., Ph.D.	101	657
57. A Bunsen burner for acetylene. By A. E. Munby, M.A.	103	—
58. The reactions between lead and the oxides of sulphur. By Henry C. Jenkins and Ernest A. Smith	104	666
59. X Ray photographs of solid alloys. By C. T. Heycock, F.R.S., and F. H. Neville	105	—
May 20th.		
60. The theory of osmotic pressure and the hypothesis of electrolytic dissociation. By Holland Crompton	109	925
61. Molecular rotations of optically active salts. By Holland Crompton	111	946
62. Heats of neutralisation of acids and bases in dilute aqueous solution. By Holland Crompton	111	951
63. A comparative crystallographical study of the normal selenates of potassium, rubidium, and cæsium. By A. E. Tutton.	115	846
64. The platinum-silver alloys; their solubility in nitric acid. By John Spiller	118	—
65. Dalton's law in solutions. The molecular depression of mixtures of non-electrolytes. By Meyer Wilderman, Ph.D.	119	743
66. The action of bromdiphenylmethane on ethyl sodacetoacetate. By G. G. Henderson, D.Sc., M.A., and M. A. Parker, B.Sc.	119	676
June 3rd.		
67. On the thermal phenomena attending the change of rotatory power of freshly prepared solutions of certain carbohydrates; with some remarks on the cause of multirotation. By Horace T. Brown, F.R.S., and Spencer Pickering, F.R.S.	129	756
68. On the thermo-chemistry of carbohydrate-hydrolysis: (I) The hydrolysis of starch by vegetable and animal diastase. (II) The hydrolysis of cane-sugar by invertase. By Horace T. Brown, F.R.S., and Spencer Pickering, F.R.S.	130	783
69. Optical inversion of camphor. By Frederic Stanley Kipping, Ph.D., D.Sc., and William Jackson Pope	132	956
70. Derivatives of camphoric acid. Part II. Optically inactive derivatives. By F. Stanley Kipping, Ph.D., D.Sc., and William Jackson Pope	133	962

	Page in Proceedings.	Page in Transactions.
71. Racemism and pseudoracemism. By F. Stanley Kipping, Ph.D., D.Sc., and William Jackson Pope	135	989
72. Note on some new gold salts of the solanaceous alkaloids. By H. A. D. Jowett, D.Sc.	136	679
73. Production of camphenol from camphor. By J. E. Marsh, M.A., and J. A. Gardner, M.A.	137	—
74. Preliminary note on the oxidation of fenchene. By J. A. Gardner and G. B. Cockburn	137	—
75. Apiin and apigenin. By A. G. Perkin	138	805
76. Rhamnazin. By A. G. Perkin and H. W. Martin	139	818
77. Experimental verification of van't Hoff's constant in very dilute solutions. By Meyer Wilderman, Ph.D.	139	796
78. The isomeric dibromethylenes. By Thomas Gray, B.Sc.	140	1023
June 17th.		
79. Molecular refraction of dissolved salts and acids. Part II. By J. H. Gladstone, D.Sc., F.R.S., and W. Hibbert	141	822
80. On a space formula for benzene. By J. Norman Collie, Ph.D., F.R.S.	143	1013
81. On the production of some nitro- and amido oxylepidolines. By A. Lapworth, D.Sc., and J. Norman Collie, Ph.D., F.R.S.	146	838
82. Further experiments on the absorption of moisture by deliquescent substances. By H. Wilson Hake, Ph.D.	147	—
83. The fusion point, boiling point, and specific gravity of nitrobenzene. By R. J. Friswell	147	1010
84. The action of light on a solution of nitrobenzene in concentrated sulphuric acid. By R. J. Friswell	148	—
85. The reduction of perthiocyanic acid. By F. D. Chattaway, M.A., and H. P. Stevens, B.A.	149	833
86. The so-called hydrates of isopropyl alcohol. By T. E. Thorpe, LL.D., F.R.S.	150	920
87. The carbohydrates of the cereal straws. By C. F. Cross, E. J. Bevan, and Claud Smith	150	1001
88. Studies on the constitution of tri-derivatives of naphthalene No. 16. Conversion of chloronaphthalene-disulphonic acids into dichloronaphthalenesulphonic acids. By Henry E. Armstrong and W. P. Wynne	152	—
89. Conversion of 1 : 1′- into 1 : 4′-dichloronaphthalene by hydrogen chloride. The products of hydrolysis of 1 : 1′-dichloronaphthalene-3-sulphonic acid. By Henry E. Armstrong and W. P. Wynne	154	—
90. Note on the formation of diacetanilide. By Georg Young, Ph.D.	156	—
91. Derivatives of phenetol azo-phenols. By J. T. Hewitt, M.A., D.Sc., Ph.D., T. S. Moore, and A. R. Pitt	157	—
92. 3-Ketopinic acid and camphoic acid. By W. S. Gilles and F. F. Renwick	158	—
93. Note on stereoisomeric di-derivatives of camphor, and on nitro-camphor. By T. M. Lowry, B.Sc.	159	—

	Page in Proceedings.	Page in Transactions.
94. The interaction of ethylene dichloride and ethylic sodiomalonate. By Bevan Lean, D.Sc., B.A., and Frederic H. Lees	160	1062
95. Hexanaphthene and its derivatives. Preliminary note. By Emily C. Fortey, B.Sc.	161	—
Papers received during vacation and published in Transactions.		
96. The ethers of camphor oxime. By M. O. Forster, Ph.D.	165	1030
97. The action of nitrogen trioxide and tetroxide on alcohols. Part I. By Julius Berend Cohen, Ph.D., and Harry Thornton Calvert, B.Sc.	166	1050
98. The action of nitrogen tetroxide on ortho- and para-nitrobenzylalcohol. By Julius B. Cohen, Ph.D., and William H. Harrison, B.Sc.	166	1057
99. The action of aromatic amines upon diacetyltartaric anhydride. By Julius Berend Cohen, Ph.D., and William Hudson Harrison, B.Sc.	167	1060
100. Studies on citrazinic acid. Part V. By W. J. Sell, M.A., and F. W. Dootson, B.A.	167	1068
101. The condensation of chloral with resorcinol. II. By J. T. Hewitt, M.A., D.Sc., and Frank G. Pope	167	1084
102. On β-oxycellulose. By Benjamin Samuel Bull, M.A., B.Sc.	168	1090
103. A new synthesis of phloroglucinol. By David S. Jerdan, B.Sc.	168	1106
104. Phenanthrone. By Francis R. Japp, F.R.S., and Alexander Findlay, M.A., B.Sc.	169	1115
105. The yellow colouring principles of various tannin matters. IV. By A. G. Perkin	170	1131
106. Ammonia and phenylhydrazine derivatives of αβ-dibenzoylcinnamene (anhydracetophenonebenzil). By Francis R. Japp, F.R.S., and Alfred Tingle, B.Sc.	170	1138
107. Derivatives of cotoin and phloretin. By A. G. Perkin and H. W. Martin	171	1149
108. Azobenzene derivatives of phloroglucinol. By A. G. Perkin	172	1154
109. The action of phosphorus pentachloride on fenchone. By J. Addyman Gardner, M.A., and G. B. Cockburn, B.A.	173	1156
110. Ketolactonic acid and its homologues. By C. H. G. Sprankling, B.Sc.	173	1159
November 4th.		
111. On the properties of liquid fluorine. By Professors Moissan and Dewar	175	—
112. The liquefaction of air and the detection of impurities. By Professor Dewar	186	—
113. The absorption of hydrogen by palladium at high temperatures and pressures. By Professor Dewar	192	—

	Page in Proceedings.	Page in Transactions.
114. On some yellow vegetable colouring matters. By A. G. Perkin	198	1194
115. Naphthylureas. By George Young, Ph.D., and Ernest Clark	199	1200
116. Benzoylphenylsemicarbazide. Preliminary notice. By George Young, Ph.D., and Henry Annable	199	—
117. Sulphocamphylic acid. By W. H. Perkin, jun.	200	—
November 18th.		
118. On the decomposition of camphoric acid by fusion with potash or soda. By Arthur W. Crossley and W. H. Perkin, jun.	217	1*
119. Experiments on the synthesis of camphoric acid. By W. H. Bentley and W. H. Perkin, jun.	218	45*
120. Synthesis of an isomeride of camphoronic acid. By S. B. Schryver, Ph.D.	220	68*
121. The action of magnesium on cupric sulphate solution. By Frank Clowes, D.Sc., and R. M. Caven, B.Sc.	221	—
122. Properties and relationships of dihydroxytartaric acid. By Henry J. Horstman Fenton, M.A.	224	71*
123. The molecular association of liquids and its influence on the osmotic pressure. By Holland Crompton	225	—
December 2nd.		
124. The representation of the isomeric benzene hexachlorides by Collie's space-formula. By Francis Edward Matthews, Ph.D.	232	
125. Compounds of piperidine with phenols. By Otto Rosenheim, Ph.D., and Philip Schidrowitz, Ph.D.	234	139*
December 15th.		
Kekulé memorial lecture. By Professor Francis R. Japp, LL.D., F.R.S.	235	97*
December 16th.		
126. Stereochemistry of unsaturated compounds. Part I. Esterification of substituted acrylic acids. By John J. Sudborough and Lorenzo L. Lloyd	240	81*
127. Formation and hydrolysis of esters. By John J. Sudborough, Ph.D., D.Sc., and Martin E. Feilmann, B.Sc.	241	—
128. A new method of determining freezing points in very dilute solution. By Meyer Wilderman, Ph.D.	245	—
129. A possible basis of generalisation of isomeric changes in organic compounds. By Arthur Lapworth, D.Sc.	246	—

* Papers printed in the Transactions for 1898 are distinguished by an asterisk after the page number. Where no reference is given to the Transactions, the paper has appeared only in the "Proceedings."

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INDEX TO AUTHORS' NAMES.

Annable, Henry, 199.
Armstrong, Henry E., 152, 154.
Aston, Emily, 89.

Baker, Julian L., 3.
Bentley, W. H., 218.
Bevan, E. J., 150.
Brooke, Arthur, 51.
Brown, Horace T., 4, 129, 130.
Bull, Benjamin Samuel, 168.

Caldecott, W. A., 100.
Calvert, Harry Thornton, 166.
Caven, R. M., 221.
Chattaway, F. D., 87, 149.
Clark, Ernest, 199.
Clowes, Frank, 221.
Cockburn, G. B., 137, 173.
Cohen, Julius Berend, 166, 167.
Collie, J. Norman, 43, 89, 143, 146.
Cook, Ernest H., 74.
Crompton, Holland, 109, 111, 225.
Cross, C. F., 150.
Crossley, Arthur W., 21, 217.

Dewar, James, 175, 186, 192.
Dixon, Augustus Edward, 6.
Dixon, H. B., 99.
Dobbie, James J., 101.
Dootson, F. W., 167.
Dunstan, Wyndham R., 76.
Dymond, T. S., 42.

Evans, Clare de Brereton, 64.

Feilmann, Martin E., 241.
Fenton, Henry J. Horstman, 63, 224.
Findlay, Alexander, 169.
Forster, M. O , 21, 165.
Fortey, Emily C., 161.
Francis, Francis E., 63.
Frankland, Percy, 9.
French, Wm., 52, 79.
Frisw.ll, R. J., 147, 148.

Gardner, J. A., 137, 173.
Gilles, W. F., 64.
Gilles, W. S., 158.
Gladstone, J. H., 141.
Goulding, Ernest, 76.
Gray, Thomas, 140.

Hake, H. Wilson, 147.
Hanes, Edgar S., 62.
Harrison, William Hudson, 166, 167.
Hartley, W. N., 11, 46.
Hemmy, A. S., 53, 64.
Henderson, G. G., 119.
Hewitt, J. T., 157, 167.
Heycock, C. T., 60, 105.
Hibbert, W., 141.
Hughes, F., 42.

Jackson, Percy G., 20.
Japp, Francis Robert, 48, 169, 170, 235.
Jenkins, Henry C., 104.
Jerdan, David S., 168.
Jowett, H. A. D., 136.

Kay, Sydney A., 75.
Kipping, Frederic Stanley, 132, 133, 135.

Lapworth, Arthur, 146, 246.
Lawrence, W. T., 65.
Lean, Bevan, 160.
Lees, Frederic H., 160.
Ling, Arthur R., 3.
Liversidge, A., 22.
Lloyd, Lorenzo L., 20, 240.
Lowry, T. M., 159.
Lumsden, John S., 48.

Mallett, J. W., 55.
Marsden, Fred, 101.
Marsh, J. E., 137.
Martin, H. W., 139, 171.
Matthews, Francis Edward, 18, 232.
McConnell, Arthur H., 62.
Millar, J. H., 4.
Moissan, Professor, 175.
Moore, T. S., 157.
Morris, G. Harris, 4.
Munby, A. E., 103.
Myers, Henry C., 100.

Neville, F. H., 60, 105.

Parker, M. A., 119.
Perkin, A. G., 5, 53, 138, 139, 170, 171, 172, 198.
Perkin, W. H., jun., 72, 200, 217, 218.
Pickering, Spencer, 129, 130.
Pitt, A. E., 157.
Pope, Frank G., 167.
Pope, William Jackson, 11, 132, 133, 135.
Price, Thomas Slater, 9.

Ramage, Hugh, 11, 46.
Rayleigh, Lord, 17.
Renwick, F. F., 64, 158.
Rodger, J. W., 49.
Rosenheim, Otto, 234.
Ruhemann, S., 52, 53, 64.
Russell, E. J., 99.

Schidrowitz, Philip, 234.
Schryver, S. B., 220.
Scott, Alexander, 70, 71.
Sell, W. J., 167.
Shenstone, W. A., 2.
Smith, Claud, 150.
Smith, Ernest, A., 104.
Snape, H. Lloyd, 50, 51.
Spiller, John, 118.
Sprankling, C. H. G., 173.
Stevens, H. P., 87, 149.
Sudborough, John J., 19, 20, 240, 241.

Thomas, G. L., 58.
Thorpe, Jocelyn Field, 72.
Thorpe, T. E., 49, 150.
Tingle, Alfred, 170.
Titherley, A. W., 45, 46.
Tutton, Alfred, E., 10, 115.

Walker, James, 48, 75.
Wilderman, Meyer, 119, 139, 245.
Williams, Katherine I., 88.
Wynne, W. P., 152, 154.

Young, George, 53, 156, 199.
Young, Sydney, 58.

INDEX TO DISCUSSIONS.

Armstrong, H. E., 18, 59, 100, 105.

Baker, H. B., 3
Blount, B. H., 71.
Bloxam, A. G., 249.
Bone, W. A , 136.

Cassal, C. E., 89.
Collie, J. N., 249.
Craw, J. A., 59, 62.
Crookes, Sir W., 100, 192.

Dewar, James, 88, 100, 105, 107, 142, 149
Dunstan, W. R., 43, 89, 143.

Forster, M. O., 44, 220.
Friswell, R. J., 119, 145, 198.

Gladstone, J. H., 118, 185.
Green, A. G., 149.
Groves, C. E., 59, 62, 71, 88, 89, 105.

Harcourt, A. Vernon, 3, 18, 42, 59, 71, 119.
Hehner, O., 89.
Hewitt, J. T., 149, 244.
Heycock, C. T., 71.

Jenkins, H. C., 62.

Kipping, F. S., 44, 132, 145. 220, 249.

Lapworth, Arthur, 233.
Ling, A. R., 132.

McLeod, H., 18.
Morris, G. H., 4.

Newlands, J. A. R., 62.

Parry, E. J., 233.
Perkin, W. H., 184.
Pickering, S. P. U., 112, 245.

Ramsay, William, 18.
Rideal, Samuel, 48.
Roberts-Austen, W. C., 105, 106.

Scott, Alexander, 43, 100.
Shields, John, 114, 244.
Spiller, John, 71.
Sutherland, D. A., 89.
Sworn, W. A., 145.

Thorne, L. T., 3.
Thorpe, T. E., 3, 59, 185.
Tilden, W. A., 3, 145, 222.

Whetham, W. C. D., 113.
Wynne, W. Palmer, 232, 247.

INDEX OF SUBJECTS.

Acetaldoxime, derivatives of, 76.
Acetoxime, derivatives of, 77.
α-Acetyl-β-diphenylpropionic acid, preparation and properties of, 119.
Acetylene, a Bunsen burner for, 103.
Acids, fatty, Wechsler's method of separating, 22.
Acrylic acids, substituted, stereoisomeric method of distinguishing, 241.
Affinity, residual, 113.
Air, liquefaction of, 186.
Alkaloids, Solanaceous, gold salts of, 136.
Alkyl haloids, action of, on aldoximes and ketoximes, 76.
Alkyloximes, formation and constitution of, 76.
β-Alkylacetosuccinic ethers, hydrolysis of, 174.
Alkylammonium hydrosulphides, dissociation pressures of, 48.
Allylphenylthiohydantoin, preparation and properties of, 8.
Aluminium, spectrographic analysis of, 47, 48.
Aluminous minerals, spectrographic analysis of, 12.
Alums, spectrographic analysis of, 47.
Amarone, identity of, with tetraphenylazine, 51.
American petroleum, hydrocarbons from, 58.
Ammonia, action of, on solid iodine, 55.
Amyl derivatives of substituted glyceric acids, 9.
Analysis, method of spectrographic, 11, 46.
Anhydracetophenonebenzil, derivatives of, 170.
Anniversary meeting, 80.
Apigenin, constitution, composition, properties and preparation of, 54, 138.
Apiin, properties of, 53.
Apparatus, new forms of, 3.
———— for concentration of argon from air, 18.
———— for steam-distillation, 18.
Argon, concentration of, from air, 18.
Association, molecular, of liquids, 225.
———— of solvent, effect of, on osmotic pressure, 227.
Atropine, gold salts of, 137.

Bauxites, spectrographic analysis of, 12.
Benzamides, hydrolysis of substituted, 20.
———— new substituted, 21.
Benzene, a space formula for, 143.
———— hexachlorides and the space formula, 232.
———— substitution in, explanation of, 144.
Benzil, preparation of, from benzoin, 20.
———— condensation product: a correction, 48.
Benzoylphenylsemicarbazide, properties of, 199.
Benzoic acids, di-ortho-substituted, Part III, 20.
Benzylphenylthiohydantoin, preparation and properties of, 8.
Black band ores, spectrographic analysis of, 12.
Blendes, spectrographic analysis of, 13.
di-Bromethylenes, the isomeric, 140.
π-Bromocamphoric acid, inactive, preparation and properties of, 134.
Bromodihydro-β-camphylic acid, 200.
Budde's experiments on the expansion of chlorine, 3.
"Bumping" of boiling liquids, how stopped, 19.
iso-Butylhydroxycyanovaleric acid, preparation and properties of, 219.
iso-Butylmethylhydroxyglutaric acid, preparation of, 219.
Calcium present in aluminium, origin of, 48.
cis-π-Camphanic acid, inactive, preparation and properties of, 134.
trans-π-Camphanic acid, inactive and active, preparation and properties of, 134.
Camphanol, production of, from camphor, 137.

Camphenylnitramine, preparation and properties of, 21.
Camphoic acid and ketopinic acid, 65, 158.
Camphor, optical inversion of, 132.
———— stereoisomeric di-derivatives of, 159.
Camphoric acid, formula for, 218.
———— —— synthesis of, 218.
———— —— decomposition of, 217.
———— —— derivatives of, II, 133.
ψ-Camphoric acid, preparation and properties of, 218.
Camphoronic acid, synthesis of, 72.
———— —— —— an isomeride of, 220.
Camphoroxime, ethers of, 165.
Camphotricarboxylic acid and ketopinic acid, 63.
trans-Camphotricarboxylic acid, inactive, preparation and properties of, 135.
Cannizzaro, Professor, reply of, to Society's Address, 1.
Carbohydrates of cereal straws, 150.
———— thermochemistry of change of rotatory power of, 129.
Carbon, optical effects of asymmetric, 9.
——— atomic weight of, 70.
Carbon *mon*-oxide, action of "nascent" oxygen on, 99.
——— ———— completely absorbed by potash, 71.
Carbon *di*-oxide, expansion of potash solution by absorption of, 71.
Catalytic agents, interaction of highly-purified gases in presence of, 52.
Certificates of candidates for election, 25, 55, 91, 123, 206.
Chloral, condensation of, with resorcinol, II, 167.
Chlorine, behaviour of pure dry, under the silent discharge, 2.
———— anomalous expansion of, 3.
———— action of pure dry, on mercury, 3.
Chlorine peroxide, explosion of, with carbonic oxide, 99.
αα-Chlorobromocamphors, two isomeric, 159.
π-Chlorocamphoric acid, inactive, preparation and properties of, 134.
Chlorodihydro-β-camphylic acid, 200.
Chlorodiparaconic acid, preparation and properties of, 100.
Chlorofenchone phosphonic acid, preparation and properties of, 173.
α-Chloro-γ-methyl-α′-pyridinecarboxylic acid, preparation and properties of, 89.
α-Chloro-α′-methyl-γ-pyridinecarboxylic acid, preparation and properties of, 89.
: 4′-*di*-Chloronaphthalene, preparation of, 154.
di-Chloronaphthalenesulphonic acids, 152.
2 : 4′-*di*-Chloronaphthalene-2′-sulphonic acid, preparation and properties of, 153.
2 : 1′-*di*-Chloronaphthalene-3′-sulphonic acid, 153.
1 : 1′-*di*-Chloronaphthalene-3-sulphonic acid, preparation and properties of, 155.
Chlorostilbene, a new, from deoxybenzoin, 20.
Citrazinic acid : studies on, Part V, 167.
Citric acid, synthesis of, 65.
Clay ironstones, spectrographic analysis of, 12.
Cobalt ores, spectrographic analysis of, 13.
Cobalt, oxides of, and cobaltites, 62.
Cobaltous acid, properties of, 62.
Colpoon compressum, glucosides from, 170.
Commemoration Medal granted to President, 217.
Corydaline, Part V, 101.
Corydic acid, preparation and properties of, 101.
Cotoin, diazobenzene derivatives of, 172.
Curtius' compound, identical with sodium benzamide, 46.

Dalton's law in solutions, 119.
Deliquescent substances, absorption of water by, 147.
Dextrose, solution-density and cupric reducing power of, 5.
Diacetanilide, formation of, 156.
Diacetyltartaric anhydride, action of aromatic amines, 167.
Diastase, hydrolysis of starch by, 130.
———— products of the action of, on starch, 8.
Dihydrocamphoketone, preparation and properties of, 218.
Dihydrocamphoric acid, preparation and properties of, 218.
Dihydro-*iso*-lauronic acid, preparation of, 201.
Dihydroxymaleic acid and its isomeride, 224.
Dihydroxytartaric acid, preparation and properties of, 224.
αγ-Dimethyl-α′-chloropyridine, oxidation products of, 89.
Dimethylphenylthiohydantoin, preparation and properties of, 9.
Dithionic acid from sulphurous acid, 42.

Electrical conductivity, theory of, in liquids, 112.
Electric flame, oxidation of nitrogen by, 18.
Electrolytic dissociation, hypothesis of, 109.
———— reduction of a sulphuric acid solution of nitrobenzene, 149.

Ellagic acid, plants of which it is the colouring matter, 170.
Enantiomorphism of ethylpropylpiperidonium iodide, 64.
Esterification of unsaturated acids, 240 *seq.*
Esters, formation and hydrolysis of, 241.
——— rate of hydrolysis of, 242–3.
α-Ethyladipic acid, 161.
α-Ethylbutanetricarboxylic acid, preparation and properties of, 161.
Ethyleneaniline and toluidine, dinitrosamines of, 63.
Ethylic acetosuccinate, colour reaction of, 53.
——— ——— some derivatives of, 53.
Ethylic acetyl-*iso*-butylsuccinate, preparation and properties of, 219.
——— α-acetyl-β-diphenylpropionate, preparation and properties of, 119.
——— adipate, 161.
——— alcohol, action of, in formation of urea from ammonium cyanate, 75.
——— anhydro-oxalaconitate and its isomeride, 64.
——— benzoylsuccinate, properties of, 53.
——— brom-*iso*-butylacetate, properties of, 219.
——— butanetricarboxylate, 161.
——— α-chlorocrotonate, action of, on β-ketonic acids, 52.
——— chlorofumarate, action of, on β-ketonic acids, 52.
——— β-chlor-ααβ-trimethylglutarate, preparation and properties of, 73.
——— β-cyano-ααβ-trimethylglutarate, preparation and properties of, 73.
——— α-ethylbutanetricarboxylate, preparation and properties of, 161.
——— β-hydroxy-ααβ-trimethylglutarate, preparation and properties of, 72.
——— pyronetricarboxylate and its isomeride, 64.
——— sodacetoacetate, derivatives of, 119.
——— sodiomalonate and ethylene dichloride, interaction of, 160.
Ethylphenylthiohydantoin, preparation and properties of, 9.
Ethylpropylpiperidonium iodide, enantiomorphic forms of, 64,
Ethyl-*o*-tolylthiohydantoin, preparation and properties of, 9.

Fellows, election of, 57, 102, 141, 231.
Fenchene, oxidation of, 137.
Fenchone, action of phosphorus pentachloride on, 173.
Ferrous sulphide in the decomposition of iron pyrites, 100.
Fisetin, colouring matter of *Rhus rhodanthema*, 193.
Fish, cooked, composition of, 88.
Fluorine, properties of, at a low temperature, 183.
——— refractive index of, 183, 185.
——— magnetic rotation of, 184 *seq.*
——— critical point of, 177.
——— liquifying point of, 178 *seq.*
——— properties of liquid, 175 *seq.*
——— capillary constant of liquid, 181.
——— density of liquid, 180 *seq.*
Foreign Members, proposal of, 240.
Formaldoxime, derivatives of, 76.
Freezing points in dilute solution, determination of, 245.
Fumaroid linking of carbons in benzene compounds, 233.
Furfuroids in cereal straws, 151.

Galenas, spectrographic analysis of, 13.
Gallium, wide occurrence of, in minerals, 13.
Glyceric acids, amyl derivatives of substituted, 9.
Glycollic aldehyde from dihydroxymaleic acid, properties of, 63.
Gold, occurrence of, in natural saline deposits, 23.
——— determination of, in natural saline deposits, 23.
——— nuggets, crystalline structure of, 22.
Gold-sodium alloys, crystalline structure of, 106.

Hæmatites, brown and red, spectrographic analysis of, 12.
Heats of neutralisation, 111.
Helium, collection of, from Bath water, 190.
Hexanaphthene, preparation and properties of, 161.
Hydration of salts a cause of their deliquescence, 147.
Hydrocarbon in gas from Bath springs, 190 *seq.*
β-Hydroxy-ααβ-trimethylglutaric acid, preparation and properties of, 72.
Hydroxyl groups in catechin and cyanomaclurin, estimation of, 5.
Hyoscine gold salts, 137.
Hyoscyamine gold salts, 137.

Invertase, hydrolysis of cane-sugar by, 131.
Invert-sugar, solution-density, and cupric-reducing power of, 5.
Iron pyrites, decomposition of, 100.

Kekulé Memorial Lecture, 235.
Ketolactonic acid and its homologues, 173.

β-Ketonic acids. Parts III, IV, V, 52, 53, 64.
Ketopinic acid and its derivatives, 64.
δ-Ketopinic acid, properties of, 158.

Lævulose, solution-density, and cupric-reducing power of, 5.
Laurent's "amarone," preparation and properties of, 51.
iso-Lauronolic acid, properties of, 201.
iso-Lauronolic and *iso*-lauronic acids, constitution of, 202.
Lead, action of oxides of sulphur on, 104.
—— metallurgy of, 104.
Liebisch's rule for distinguishing mixtures and racemic compounds, 136.
Light, lecture illustration of chemical effect of, 149.
Limonites, spectrographic analysis of, 12.
Longstaff Medal, award of, 42, 80.
ψ-Lutidostyril, products of the interaction of, with phosphorus pentachloride, 44.

Maclurin, derivatives of, 5,
Magnesium, action of, on cupric sulphate solution, 221.
Magnesium nitride, action of, on organic compounds, 50.
Magnesium-copper couple, action of, on water, 223, 224.
Magnetites, spectrographic analysis of, 12.
Maleoid linking of carbons in benzene compounds, 238.
Maltodextrin, α- and β-, properties of, 3.
Manganese ores, spectrographic analysis of, 12.
———— sulphate, use in oxidising sulphurous acid, 42, 43.
Melting points, method of determining, 74.
Memorial Lecture, Kekulé, 235.
———— ———— Pasteur, 79.
Mercury and chlorine, interaction of pure, 3.
Methylcamphorimine from camphoroxime, preparation and properties of, 21.
Methylphenylthiohydantoin, preparation and properties of, 8.
Methyl-*o*-tolylthiohydantoin, preparation and properties of, 8.
Minerals, aqueous origin of many, 13.
Moisture, influence of, on production of ozone, 2.
Monoses, the carbohydrates of cereal straws, 151.
Multirotation, cause of, 129.
Myricetin, colouring matter of Venetian sumach, 170.

Naphthalene, tri-derivatives of, 153 *seq.*
Naphthylureas, preparation and properties of, 199.
Nickel ores, spectrographic analysis of, 13.
Nicotinic acids, substituted, 167.
Nitric acid, action of, on platinum-silver alloys, 118.
Nitrobenzene, some physical constants of, 147.
———— solution in sulphuric acid, action of light on, 148.
Nitrobenzylic alcohol, *o*- and *p*-, action of nitrogen tetroxide on, 166.
Nitrocamphor, preparation and properties of, 160.
Nitrogen gas, oxidation of, 17.
———— iodide, composition of, 55.
———— *tri*- and *tetr*oxide, action of, on alcohols, 166.
———— *tetr*oxide, action of, on nitrobenzylic alcohols, 166.
Nomination for President, 69.
Non-electrolytes, molecular depression of mixtures of, 119.

Officers and Council, changes in, 41.
"Optical antipodes," 133.
Optical effects of asymmetric carbon in glycerates, 9.
Organic compounds, isomeric changes in, 246.
Osmotic pressure, theory of, 109.
———— ———— and association, 225.
Osyritin, from Cape sumach, 170.
β-Oxycellulose, derivatives of, 168.
Oxygen, behaviour of, under the silent discharge, 2.
Oxypicolines, some nitro- and amido-, 146.
Ozone, conversion of oxygen into, under the silent discharge, 2.
———— unstable in contact with an alkali, 3.

Palladium, absorption of hydrogen by, 192.
Palladium-hydrogen, latent heat of dissociation of, 197.
Pasteur Memorial Lecture, 79.
Pentane and *iso*-pentane from American petroleum, 58.
———— physical constants of, 58.
———— fractionation of, 60.
Perthiocyanic acid, hydrolysis, of, 87.
———— ———— reduction of, 149.
Phenanthrone, constitution of, 169.
β-Phenanthrylamine, formation of, 169.

β-Phenanthrylic acetate, formation of, 169.
β-Phenanthrylic oxide, formation of, 169.
o-Phenetolazophenol, *o*- and *p*-, preparation, properties and derivatives of, 157.
o-Phenetolazophenyl benzoate, properties of, 157.
p-Phenetolazophenyl acetate and benzoate, properties of, 158.
o-Phenetolazophenylbenzene, properties of, 157.
p-Phenetolazophenylbenzene sulphonate, properties of, 158.
Phenylethoxytriazole carboxylates, properties of, 53.
Phenylstyrenyloxytriazole, oxidation of, 53.
Phloretin, diazobenzene derivatives of, 172.
Phloroglucinol, synthesis of, 168.
———— azobenzene derivatives of, 172.
Phloroglucinoldisazobenzene-*m*-azonitrobenzene, preparation and properties of, 173.
Phloroglucinol-*o*-trisazoanisol, preparation and properties of, 172.
Phloroglucinol-trisazobenzene, preparation and properties of, 172.
Phosphorus in cooked fish, 89.
———— pentachloride as an agent for replacing the sulphonic radical by chlorine, 152.
Photography, use of trioxypicoline in, 146.
Pinophanic acid from ketopinic acid, 65.
Piperidine, compounds of, with phenols, 234.
Platinum nuggets, crystalline structure of, 22.
Platinum-silver alloys, solubility of, 118.
Potassium ethylamide, preparation and properties of, 45.
Pressure, partial, of dissolved gases, 226.
Prior's "achroodextrin III," 3.
iso-Propyl alcohol, "hydrates" of, 150.
"Pseudo-racemism," 135.
Pyridine derivatives from the distillation of ethylic β-amido-crotonate, 43.
Pyridine-benzene formula, 239.
Pyrites, spectrographic analysis of, 13.

Racemism and pseudo-racemism, 135.
Refraction constants of crystalline salts, 10, 11.
———— substances having two-indices of, 141.
Refraction, molecular, of dissolved salts and acids, 141.
Research Fund, donation of 1,000 guineas, 24.
Resorcinol, condensation of chloral with, II, 167.
Rhamnazin, constitution and properties of, 139.
Rhus rhodanthema, colouring matter of, 198.
Rotation, molecular, of optically active salts, 111.
———— specific, always constant for the same substance, 142.
Rubidamide, preparation and properties of, 46.

Saline deposits, occurrence of gold in, 23.
Selenates of potassium, rubidium, and cæsium, crystallography of, 115.
Siderites, spectrographic analysis of, 12.
Silver-platinum alloys, solubility of, 118.
Sodamide, reaction of, with organic substances, 45.
———— substitution derivatives of, 45.
———— constitution of substituted, 46.
Sodium-gold alloys, crystalline structure of, 106.
Solvents, associated or monomolecular, 110.
Starch, products of the action of diastase on, 3, 130.
Stassfurt minerals, spectrographic analysis of, 47.
Statistics of Society, 81.
Stereochemistry of unsaturated compounds, I, 240.
Substances, pure, properties of some, 2.
Sugar, new synthesis of a, 68.
Sulphates, mixed, of the vitriol group, 71.
Sulphocamphylic acid, derivatives of, 200.
Sulphurous acid, titration of, by permanganate, 42.
Sumach, Cape and Venetian, colouring matters of, 170.

Temperature, influence of, on rotation, 10.
Tetraphenylazine, identity of, with amarone, 51.
Tetraphenylenefurfuran, formation of, 169.
Thermal effects attending change of rotatory power, 130.
Thermochemistry of carbohydrate hydrolysis, 130.
Thiohydantoins, chemistry of, 6.
———— nomenclature of, 9.
Tin ores, spectrographic analysis of, 13.
Toluene, nitration of, 145.

Toluidine and ethyleneaniline, dinitroamines of, 63.
o-Tolylthiohydantoin, preparation and properties of, 8.
Triacetylmaclurinazobenzene, preparation and properties of, 5.
aaβ-Trimethylglutaconic acid, preparation and properties of, 72.
aaβ-Trimethylgluteric acid, preparation and properties of, 72.
aaβ-Trimethyltricarballylic acid, 73.
Trioxypicoline, preparation and properties of, 146.
Triphenylhydroxypyrrholone, formation and properties of, 171.
1 : 3 : 4-Triphenylpyrazole, formation of, 171.
Triphenylpyrrhole, formation of, 171.
Tustin, Mr., Donation to Research Fund of 1,000 guineas, 24.

Urea formation, velocity of, in aqueous alcohol, 75.

Van't Hoff's constant in dilute solutions, 139.
Viscosity of mixtures of miscible liquids, 49.
——— numbers proposed as a test of identity, 59.

Water, ultra-violet spectrum of, as test for presence in flames, 190.
Wechsler's method of separating fatty acids, 21.
Wein's reduction tables, correction of, 3.

X-ray photographs of solid alloys, 105.
X-rays, opacity of elements to, relation of, to atomic weights, 107.

Zinc alloys, freezing point curves of, 60.
Zinc-platinum couple for stopping "bumping," 19.

ERRATA.

Page.	Line.	
42	7	*for* "dithonic" *read* "dithionic."
65	24	,, "Laurance" *read* "Lawrence."
89	34	,, "α-chloro-α-methyl-α'-pyridine carboxylic acid" *read* "α-chloro-α'-methyl-γ-pyridine carboxylic acid."
119	12	,, "impurities" *read* "sulphuric acid."

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PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

EDITED BY THE SECRETARIES.

No. 178. Session 1896–7.

January 21st, 1897. Mr. A. G. Vernon Harcourt, President, in the Chair.

Messrs. Charles A. Hill, Arthur Marshall and William H. Sodeau were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. William Arbuckle, 34 Moore Street, Cadogan Square, S.W.; Masumi Chikashigé, B.Sc., Kumamoto, Japan; Alfred Foster Cholerton, Lyndum House, Lincoln Street, Leicester; Clarence Hamilton Creasey, 78 Baggeholme Road, Lincoln; James Crowther, B.Sc., West Field, Lightcliffe, Halifax; William Alfred Davis, 108 Gordon Road, Peckham, S.E. Ernest Goulding, 18 Mercer's Road, Holloway, N.; Charles Heppenstall, Ferrybank, Arklow, Co. Wicklow; Harold Johnson, 5 Boulevard Clovis, Bruxelles; William Robert Lang, B.Sc., 5 Crown Gardens, Glasgow; Barker North, 3 Manor Terrace, Felixstowe; Herbert Spindler Pullar, Rosebank, Perth, N.B.; William Ralston, B.Sc., 337 Cathcart Road, Glasgow; John Stewart Remington, Dromore, Milverton, Leamington; Leonard Sumner, B.Sc., Butt Hill, Prestwich, near Manchester; Andrew Turnbull, Ph.D., Daldowie, Broomhouse, near Glasgow.

The certificates of the following candidates, recommended by the Council under Bye-law I (3), were also read:—

Thomas Hannibal Aquino, Gadag, Dharwar District, India. Alfred Rutter, Broken Hill, N.S.W. Rustomji Navroji Unwalla, Bhaunagar, Kathiawar, India.

The following is the text of the letter which has been received from Professor Stanislao Cannizzaro, acknowledging the address presented to him by the Society on the occasion of his jubilee.

To the Council and Fellows of the Chemical Society of London.

GENTLEMEN,—I beg to offer to your Society the report of the celebration of my seventieth birthday, together with the volume containing

some of my writings which were reprinted on that occasion, and a copy in bronze of the gold medal which was presented to me.

At the same time, I beg to convey to my colleagues the expression of my heartfelt gratitude for their very flattering address, which I have received with the greatest satisfaction.

The Chemical Society won my devotion, when, in 1862, they added my name to the restricted roll of their foreign members; and again in 1872 when they honoured me by intrusting to me the delivery of the Faraday Lecture.

A further proof of their high consideration is now offered to me in this address, in which I find my labours for Science appreciated and valued in so very high a degree by authority so competent: I feel I am indebted for this favourable estimate of my merits to the extreme kindness which my English colleagues have always shown to me, and for which I now desire to express my profound gratitude.

Great is the pleasure which this fresh manifestation of their affectionate esteem has afforded me, thus assuring me that their estimate of me has in no way lessened.

Your ever true and affectionate colleague,

December, 1896. STANISLAO CANNIZZARO.

Of the following Papers, those marked * were read.

***1. "Observations on the properties of some highly purified substances." By W. A. Shenstone.**

1. The author has compared the behaviour of oxygen under the influence of the silent discharge of electricity when saturated with water vapour, and when carefully dried. The results show that, contrary to the statement of previous investigators, oxygen is most freely converted into ozone when wet, and that well dried oxygen yields only a very minute percentage of ozone. The results obtained also show that the ozone in ozonised oxygen is far more stable in the presence of water vapour than in its absence. That is to say, the change by which ozone is converted into oxygen is very greatly retarded by the presence of moisture.

2. Chlorine prepared by the electrolysis of silver chloride, and also carefully purified bromine and iodine, have been dried by very thorough treatment with prepared phosphoric oxide, and then presented to the action of mercury prepared for the purpose by several distinct methods and thoroughly dried. In every case, the metal and the halogen interacted instantly and rapidly.

3. Highly purified chlorine, when submitted to the silent discharge of electricity, does not undergo condensation.

4. The abnormal expansion of chlorine which has been described by

several observers appears to depend upon the presence of impurities in the chlorine.

Incidentally, a new vacuum tap and other novel apparatus are described in this paper.

DISCUSSION.

The PRESIDENT, Mr. H. B. BAKER, and Professor TILDEN expressed their admiration of the skill and resource which Mr. Shenstone had brought to bear in investigating a difficult problem.

Dr. THORPE stated that he had witnessed Dr. Budde's experiments at Bonn, which were conducted with great care, and he had watched the expansion of chlorine under the influence of the violet and ultra-violet rays. The chlorine had been prepared by the oxidation of hydrochloric acid, and was believed to be pure. Some subsequent observers had confirmed Dr. Budde's results, but others had failed to do so—as was now the case with Mr. Shenstone, whose painstaking enquiry, he hoped, might be the means of finally settling the question.

Dr. THORNE stated that he had observed on a large scale the instability of ozone when in contact with an alkali.

Mr. SHENSTONE, in reply, stated that he did not doubt the correctness of Dr. Budde's observations with chlorine prepared and purified as he had described. He considered, however, that such chlorine could not be regarded as highly purified, and that moisture was almost certainly present.

***2. "The action of diastase on starch." By Arthur R. Ling and Julian L. Baker.**

The authors show that maltose when heated with Fehling's solution, under the conditions prescribed by Wein, reduces 1·079 grams of copper per gram of sugar. The table of Wein, therefore, gives results which are 4·5 per cent. too low, a result also arrived at by Brown, Morris and Millar.

They have examined in detail the products of the limited action of diastase on starch at 70°, and have separated maltose and the following unfermentable substances, which were purified to such an extent as to free them from all extraneous matter.

Maltodextrin α, $C_{36}H_{62}O_{31}$, identical with Brown and Morris's maltodextrin, but having the properties $[\alpha]_D = 180$: R = 32·81.

Maltodextrin β, $C_{24}H_{42}O_{21}$, identical with Prior's "achroodextrin III," and having the properties $[\alpha]_D = 171·6$ and R = 43.

A substance, $C_{12}H_{22}O_{11}$, isomeric with maltose, and obtained from the unfermentable residue of that particular fraction previously called isomaltose by Lintner. It had the constants $[\alpha]_D = 156$ and R = 62·5, and may consist of the simple "dextrin," $C_{12}H_{20}O_{10} + H_2O$, the existence of which the authors' previous work foreshadowed. Inasmuch as

it gave a small amount of crystalline osazone, it perhaps contained maltose.

When the three substances above named are treated with an excess of diastase at 60° for a few hours, the approximate reducing powers of the products are R = 90; 91·5; 94, respectively.

There are now ample data to conclude that starch, when hydrolysed by diastase, is converted into a series of maltodextrins of gradually decreasing molecular weight and optical rotatory power, and of increasing reducing power. These appear to have the optical and reducing properties of mixtures of the original starch and maltose.

Discussion.

Dr. G. H. Morris regretted that Messrs. Ling and Baker had given no particulars of the substances they described beyond the constants $[\alpha]_D$ and R. He had therefore no means of judging whether the substances agreed with the maltodextrin described by Mr. H. T. Brown and himself, nor was it possible to follow the authors' line of work. The constants given for maltodextrin α agreed fairly with the law of definite relation as formulated by Mr. Brown and himself; but the maltodextrin β (Prior's achroodextrin III) did not, and the purity of this substance is therefore doubtful. He wished to learn more about the unfermentable residue of isomaltose, which the authors appeared to regard as one of the end-products of the action of diastase on starch. He did not think it necessary to enunciate a new theory of starch-conversion whilst there was still so much dispute as to facts.

Mr. Ling, in reply to Mr. Chapman, said he saw no reason for assuming the presence of a "stable" dextrin among the products of starch-hydrolysis; ultimately maltose was the sole product. In reply to Dr. Morris, he said that much more information would be found in the paper than it had been possible to give an account of in the brief time at his disposal. It would be seen that the formulæ of the maltodextrins could *not* be calculated from the percentages of apparent maltose which they yielded.

***3. "The solution density and cupric-reducing power of dextrose, lævulose and invert-sugar." By Horace T. Brown, F.R.S., G. Harris Morris, Ph.D., and J. H. Millar.**

The authors have extended the methods described in their previous paper (Proc., 1896, 12, 241) to the examination of the solution density and cupric-reduction of dextrose, lævulose, and invert-sugar. They find that the solution densities of the two former differ considerably with the same concentration of the solution, but that the volume occupied in solution by a unit of weight of each is less at lower than at higher concentrations, consequently the divisor to be applied to the

specific gravity decreases with the concentration. The solution density of invert-sugar was calculated from those of dextrose and lævulose, and the results so obtained were confirmed at various points by direct experiments.

They also find that the cupric-reducing powers of the three sugars, when determined under their standard conditions, are, for dextrose, $\kappa =$ 117 to 105; for lævulose, $\kappa = 107{\cdot}5$ to 101; and for invert-sugar, $\kappa =$ 111 to 103. The higher numbers are obtained when a small amount of cuprous oxide is precipitated, and the lower when reduction is carried nearly to the maximum. When the experimental numbers are expressed in the form of a curve, it is found that at the one end, taking the cupric-reduction of dextrose at 100, lævulose is represented by 91·3, and invert-sugar by 94·2; at the other end of the curve, the ratio is 100, 94·6, and 97·5; whilst at an intermediate point, which corresponds to the amount of cuprous oxide usually reduced, the relation is, dextrose 100, lævulose 92·3, and invert-sugar 96·15.

4. "Derivatives of maclurin, Part II." By A. G. Perkin.

From maclurin which yields a pentabenzoyl derivative (König and Kostanechi, *Ber.*, 1894, **27**, 1996), a pentacetyl compound has not yet been obtained, for by acetylisation in the ordinary way only sticky products result, and when excess of sodium acetate is employed (Ciamician and Silber, *Ber.*, 1894, **27**, 1628), there is formed a peculiar substance having the composition of pentacetyl maclurin less 1 molecule of water. Judging from the stability of maclurin-azo-benzene, $C_{13}H_8O_6(N_2{\cdot}C_6H_5)_2$, described in a previous communication (Bedford and Perkin, Trans., 1895, **67**, 933), when compared with that of maclurin itself, it appeared probable that this on acetylisation might behave normally, which was found to be the case.

Triacetyl-maclurin-azobenzene, $C_{13}H_5O_6(C_2H_3O)_3(N_2{\cdot}C_6H_5)_2$, orange-yellow needles, m. p. 240—243°, is insoluble in cold alkaline solutions, but decomposed by them on boiling. Suspended in acetic acid and treated with sulphuric acid, a quantitative yield of maclurin-azobenzene is produced. Phloroglucin-azobenzene similarly yields a *monacetyl* derivative, $C_6H_3O_3(C_2H_3O)(N_2C_6H_5)_2$, orange-red needles, m. p. 222—223°, also quantitatively decomposed by sulphuric acid into the azo-compound. These substances furnished no higher acetyl derivatives, two hydroxyls present in the original molecules of maclurin and phloroglucinol having assumed in their diazobenzene compounds the ketonic condition. This method is being applied for the estimation of hydroxyl groups in certain analogous substances, particularly catechin and cyanomaclurin, which combine readily with diazobenzene, but do not give normal products on acetylisation by the usual method.

Mention is made of a second product closely resembling luteolin

trimethyl ether, and formed at the same time, during the methylation of luteolin. This, though isolated many months since, was not mentioned at the time, believing that the work then published was sufficient to establish priority for the further study of this reaction. The author wishes to reserve this to himself for further examination.

5. **"Halogen-substituted acidic thiocarbimides and their derivatives; a contribution to the chemistry of the thiohydantoïns." By Augustus Edward Dixon, M.D.**

Continuing his previous work on the acidylthiocarbimides (Trans., 1895, 67, 1040; 1896, 69, 855; *ibid.*, 1593, etc.), the author endeavoured to prepare halogen substitution derivatives of certain members of the fatty acid class, in the hope that, by combination with organic bases, glycolylthioureas would be obtained of known structure, whose relations to the thiohydantoïns produced by other methods would serve to decide the constitution of the latter.

The derivatives in question were obtained by heating a mixture of sand and lead thiocyanate with the α-halogenised acid chloride (or bromide), dissolved in anhydrous toluene; as a rule, the yield amounted to only about 60 per cent. of the theoretical. On bringing the products into contact with primary (or secondary) amines, interaction occurred spontaneously, with elimination of the halogen, and formation of the corresponding substituted thiohydantoïn, for instance—

$$CH_2Cl\cdot CO\cdot NCS + ToNH_2 = HCl + \begin{matrix} CH_2\cdot S \\ | \\ CO\cdot NH \end{matrix} > C{:}NTo.$$

By prolonged boiling with hydrochloric acid, the latter compound is hydrolysed, ammonia being formed, together with a substance (melting at 119—120°), identical with the 'orthotolylthiocarbimidoglycolide' obtained by Völtzkow (*Ber.*, 1880, 13, 1580) from EtOH,ToNCS and $CH_2Cl\cdot COOH$. Since the nitrogenised organic group, introduced by the base in the formation of the thiohydantoïn, does not form an integral portion of its ring, whilst, on the other hand, the nitrogen withdrawn by hydrolysis holds no organic radicle in combination, it follows that the ring must exchange its NH for oxygen, thereby becoming $\begin{matrix} CH_2\cdot S \\ | \\ CO\cdot O \end{matrix} > C{:}NTo$; thus, by an entirely different method, the formula is corroborated, which Evers assigns to the corresponding phenyl derivative (*Ber.*, 1888, 21, 975). From orthotolylthiourea and ethylic chloracetate, a thiohydantoïn was obtained, agreeing in properties with that produced from the thiocarbimide; on hydrolysis, it afforded the same glycolide, of m. p. 119—120°.

On the other hand, thiourea, when treated with a substituted chloracetamide (*e.g.*, chloracetanilide) yielded (P. Meyer, *Ber.*, 1877, 10,

1965) thiohydantoïn, together with a substitution derivative: the phenylthiohydantoïn so obtained was apparently identical with that produced from phenylthiourea and ethylic chloracetate. The essential interaction he explained substantially as follows.

$$\begin{matrix}CH_2Cl\\|\\CO\cdot NHPh\end{matrix} + \begin{matrix}HS\\|\\NH_2\end{matrix} > C{:}NH = HCl + \begin{matrix}CH_2\cdot S\\|\\CO\cdot NPh\end{matrix} > C{:}NH,$$

and the fact that ammonia and phenylthiocarbimidoglycolide were formed on hydrolysis, appeared to agree satisfactorily with the above view of its constitution, as well as to fix that of the glycolide,

$$\begin{matrix}CH_2\cdot S\\|\\CO\cdot NPh\end{matrix} > C{:}NH + H_2O = NH_3 + \begin{matrix}CH_2\cdot S\\|\\CO\cdot NPh\end{matrix} > CO.$$

It would seem, however, from Meyer's paper, that the particular phenylthiohydantoïn obtained from chloracetanilide was not used in preparing the related phenylthiocarbimidoglycolide; it was conceivable, therefore, that the former might, though melting at the same temperature, be really isomeric with that produced by the other methods. This could be ascertained by examining the products of hydrolysis, for the withdrawal from the ring of its nitrogenised group would afford aniline, together with 'thiocarbimidoglycolide,' $\begin{matrix}CH_2\cdot S\\|\\CO\cdot O\end{matrix} > C{:}NH$; whilst, even if the phenyl group should be retained, and ammonia formed instead, the product, $\begin{matrix}CH_2\cdot S\\|\\CO\cdot NPh\end{matrix} > CO$, would still be an isomeride of the true phenyl thiocarbimidoglycolide,

$$\begin{matrix}CH_2\cdot S\\|\\CO\cdot O\end{matrix} > C{:}NPh.$$

But, on experiment, the products of hydrolysis, and hence the thiohydantoïn itself, were found to be identical with those obtained in other ways. Finally, the compound was decomposed by carbon disulphide at 180°, phenylthiocarbimide being obtained, together with rhodanic acid, but not a trace of thiocyanic acid; and hence the interaction follows the course

$$\begin{matrix}CH_2\cdot S\\|\\CO\cdot NH\end{matrix} > C{:}NPh + CS_2 = \begin{matrix}CH_2\cdot S\\|\\CO\cdot NH\end{matrix} > CS + PhNCS.$$

The author therefore regards the known monosubstituted thiohydantoïns in which the radicle is attached to nitrogen, as constituted on the type, $\begin{matrix}CH_2\cdot S\\|\\CO\cdot NH\end{matrix} > C{:}NR$; and suggests that the formation of the phenylic member from thiourea and chloracetanilide may be due to a

secondary action, for thiohydantoïn is also produced, together with aniline,

$$\begin{matrix}CH_2Cl\\ |\\ CO\cdot NHPh\end{matrix} + \begin{matrix}HS\\ |\\ NH_2\end{matrix}\!\!>C{:}NH = PhNH_2 + \begin{matrix}CH_2\cdot S\\ |\\ CO\cdot NH\end{matrix}\!\!>C{:}NH + HCl;$$

and from these, by mutual interaction, ammonia and phenylthiohydantoïn might result. Ammonia was, in fact, expelled, when aniline and thiohydantoïn were heated together, with alcohol; and a substance produced, which appeared, judging from its melting point, to be its phenylic derivative, but the quantity obtained was insufficient for analysis.

The following compounds are described:

Orthotolylthiohydantoïn, $\begin{matrix}CH_2\cdot S\\ |\\ CO\cdot NH\end{matrix}\!\!>C{:}NC_7H_7$.—From chloracetylthiocarbimide and orthotoluidine; white prisms, melting at 144—145° (corr.). When boiled with baryta-water, it yields thioglycollic acid; by boiling, dilute hydrocloric acid, it is slowly decomposed into ammonia and 'ortholylthiocarbimidoglycolide,' $\begin{matrix}CH_2\cdot S\\ |\\ CO\cdot O\end{matrix}\!\!>C{:}NC_7H_7$.

The same thiohydantoïn is produced from orthotolylthiourea and ethylic monochloracetate; its *hydrochloride* melts at 212·5—213·5° (uncorr.).

Methylphenylthiohydantoïn, $\begin{matrix}CH_2\cdot S\\ |\\ CO\cdot N\end{matrix}\!\!>C\cdot N(CH_3)C_6H_5$.—From the thiocarbimide and methylaniline; flattened needles, melting at 129—130° (corr.), and decomposed by boiling with caustic akali or baryta-water, into ammonia, methylaniline, and thioglycollic acid. It is also obtained by heating *aa*-methylphenylthiourea, in alcohol, with ethylic monochloracetate; the *hydrochloride* melts at 193—194°.

Benzylphenylthiohydantoïn, $\begin{matrix}CH_2\cdot S\\ |\\ CO\cdot N\end{matrix}\!\!>C\cdot NPh\cdot CH_2\cdot Ph$. From benzylaniline; it melts at 118—119°, and is decomposed by prolonged boiling with hydrochloric acid, into benzylaniline, and a substance melting at about 123—124°, probably 'thiocarbimidoglycolide.'

Allylphenylthiohydantoïn.—From allylphenylthiocarbamide and monochloracetamide, an oil was obtained; it appears to be a mixture of the two forms, $\begin{matrix}CH_2\cdot S\\ |\\ CO\cdot NAll\end{matrix}\!\!>C{:}NPh$ and $\begin{matrix}CH_2\cdot S\\ |\\ CO\cdot NPh\end{matrix}\!\!>C{:}NAll$.

α-Bromopropionylthiocarbimide, $CH_3\cdot CHBr\cdot CO\cdot NCS$, when treated with orthotoluidine, affords *methylorthotolylthiohydantoïn*,

$$\begin{matrix}CH_3\cdot CH\cdot S\\ |\\ CO\cdot NH\end{matrix}\!\!>C{:}NC_7H_7.$$

Crystalline powder, melting at 72—73°, and decomposed by boiling dilute alkali, with formation of α-thiolactic acid, $CH_3\cdot CH(SH)\cdot CO_2H$.

Dimethylphenylthiohydantoïn, $CH_3\cdot CH\cdot S$ / $CO\cdot N$ > $C\cdot N(CH_3)Ph$. From the above thiocarbimide and methylaniline; vitreous plates, melting at 129—130°.

α-Bromobutyrylthiocarbimide, $CH_3\cdot CH_2\cdot CHBr\cdot CO\cdot NCS$, by combination with aniline, yielded *ethylphenylthiohydantoïn*,

$$CH_3\cdot CH_2\cdot CH\cdot S \\ CO\cdot NH > C\cdot NC_6H_5.$$

White needles, m. p. 148—149° (corr.).

Ethylorthotolylthiohydantoïn.—A sandy, white powder, melting at 95—96°, to a turbid liquid, clearing at 98°; the *hydrochloride* forms white needles, m. p. 224—225° (corr.). When boiled with alkali, then acidified and mixed with ferric chloride, followed by ammonia, a purplish coloration is produced, due, probably, to the presence of α-thiobutyric acid.

For greater convenience and precision in naming 'thiohydantoïns' of the above types, and the corresponding derivatives of $CS<^{NH\cdot CH_2}_{NH\cdot CO}$, together with the related 'thiohydantoïc' acids, the author proposes a modification of the nomenclature at present employed.

6. **"The amyl (secondary butyl-methyl) derivatives of glyceric, diacetylglyceric, and dibenzoylglyceric acids, active and inactive." By Percy Frankland, Ph.D., B.Sc., F.R.S., and Thomas Slater Price, B.Sc.**

The authors describe the preparation and properties of amyl (lævo-active) glycerate (dextro-active), amyl (inactive) glycerate (dextro-active), amyl (lævo-active) glycerate (inactive), as well as of the corresponding diacetyl and dibenzoylglycerates. The interest attaching to these bodies depends, firstly, on those compounds with the inactive amyl and active acid radicle filling gaps in the series of active glycerates, diacetylglycerates, and dibenzoylglycerates already prepared, and described by one of the authors. The position of the maximum rotation in these series becomes thus more precisely localised. Secondly, the influence of one asymmetric carbon atom on another in the same molecule can be ascertained, and the principle of the superposition of the optical effects of the asymmetric carbon atoms is put to the test and found to hold good. Thus the authors show how the optical properties of the eight possible active amylglycerates can be calculated from a knowledge of the optical properties of two particular ones, and similarly in the case of the eight active amyl diacetylglycerates, and the eight active amyl dibenzoylglycerates.

In the series of the dibenzoylglycerates, of which now the methyl

ethyl, propyl, and amyl terms are known, the rotation diminishes from the methyl to the amyl compound, and there is every probability that in this series the rotation will be found to pass through a minimum.

The influence of temperature on the rotation of all the compounds described has been also investigated, with the result that, as before, the rotation of the glycerates was found to be but little sensitive to temperature, the rotation of the diacetylglycerates much more sensitive, and that of the dibenzoylglycerates still more sensitive to temperature. Again, as before, it was found that the negative rotation of the diacetylglycerates increased, whilst the positive rotation of the dibenzoylglycerates diminished with rise of temperature. It was, however, further found that the compounds in which the amyl alone was active, viz., amyl (lævo-active) glycerate (inactive), amyl (lævo-active) diacetylglycerate (inactive), and amyl (lævo-active) dibenzoylglycerate (inactive) had their rotation practically unaffected by temperature, the sensitiveness to temperature being thus confined to the rotation dependent on the asymmetric carbon atom belonging to the glyceric acid part of the molecule.

7. "The refraction constants of crystallised salts." By Alfred E. Tutton.

This communication is a reply to certain criticisms of Pope (Trans., 1896, **69**, 1530) concerning the author's work on the refraction constants of the sulphates and double sulphates containing potassium, rubidium, and cæsium (Trans., 1896, **69**, 502). It is first shown that the claim of Pope to originality, in showing that the molecular refractions of solid salts are the sums of the atomic or equivalent refractions of the components, is unfounded, and that the whole of the conclusions published in the author's memoir, with regard to this subject, in connection with the entire twenty-two double sulphates investigated, were based upon the assumption of this rule. The second point is with regard to the criticism that the mean molecular refractions of the salts given were not the mean of the three values corresponding to all three refractive indices of the biaxial crystals in each case, but the mean of the two extreme values; and with regard to the recalculated results presented by Pope taking the intermediate value into account, which Pope appears to show exhibit far greater accordance than the author's values. The author points out that the course pursued was taken after careful consideration, with full knowledge of the problem, and for the sufficient reason that the whole of the salts in question were so extremely feebly doubly refractive, and the extreme values consequently so close together, that he judged that the difference between the results of the two processes would be within the range of

experimental error. He then shows that grave errors occur in Pope's recalculations; there are numerous errors in table III, two of them being whole numbers, one of which amounts to a fifth of the total value, and table IV is entirely wrong in consequence. When the errors are corrected, the latter table, in which the two whole-number errors also appear, assumes quite a different aspect, the results of the two modes of calculation become nearly identical, the differences between them being then well within the range of the experimental error, and amply justify the author's course. The author finally shows that the two cases, rubidium sulphate and cæsium sulphate, quoted by Pope as adverse to the author's statement that "the matter in a crystal has, for refraction purposes, the same average effect as the same matter uncrystallised," lead to diametrically opposite conclusions; and, moreover, that such conclusions are of no value, as the differences in question between the values for solution and for the crystallised condition are well within the range of experimental error.

8. "The refraction constants of crystalline salts: A Correction." By William Jackson Pope.

The author regrets to find, notwithstanding that the numbers used in his paper (Trans., 1896, **69**, 1530) were several times checked, an error of a unit in two numbers in table III which vitiates the first line of table IV (*loc. cit.*, p. 1537); the first, third, seventh, and ninth numbers in the line in question should be 5·11, 5·26, 14·5, and 15·00, and in the fourth column of table III the numbers 4·25 and 13·51 should each be increased by unity. The comparison made in the six lines following table IV is consequently unjustifiable.

The error, although to be regretted, in no way affects the general argument, but, if left uncorrected, tells unfairly against the method of calculation used by Tutton.

9. "On the wide dissemination of some of the rarer elements and the mode of their association in common ores and minerals." By W. N. Hartley, F.R.S., and Hugh Ramage.

By means of spectrographic analysis the authors have examined about 170 specimens of ores and minerals, comprising oxides, carbonates, and sulphides. Half a gram of each substance, finely powdered, was heated in the oxyhydrogen flame. The following elements and their compounds yield spectra under these conditions which are easily observed.

(*a*) In very small quantity—

Na, Ca, Pb, Ni, K, Se, Bi, Cu, Ba, Cr, Rb, Ga, Mn, Ag, In, Fe, Cs, Tl, Co.

(*b*) In small quantity—

Li, Au, Cd, Sb, and Sn.

(*c*) In such quantity as to indicate that the substance is a principal constituent of the mineral—

Be, B, Di, Te, Rh ?, Mg, Al, S, Pd ?, Zn, Ce, Se, Ru ?.

Some of the metallic elements in the list (*c*) under special conditions yield oxyhydrogen flame spectra, which are easily observed even in small quantity. Other elements than the above have not been sought for in this research.

In almost every case the locality from which the specimens of ores and minerals came is recorded, and the results of the spectrographic analysis have been tabulated. Several novel and interesting facts are disclosed, which may be stated very briefly as follows.

Clay iron-stones and black-band ores.—Fifty-one specimens examined. All contain sodium, potassium, copper, calcium, and manganese; 47 contain silver; 32, lead; 21, gallium; 13, nickel; 12, chromium; 1, strontium; and 1, thallium. Probably all contain rubidium, but it is difficult to recognise owing to the multitude of iron lines. Three specimens undoubtedly contain it.

Brown hæmatites.—Six specimens examined. All contain sodium, potassium, copper, calcium, and manganese; 5 contain silver; 5, lead; and 5, nickel; 3, chromium; 2, gallium; 2, thallium: and 1, indium. Probably all contain rubidium; in one it is undoubtedly present.

Limonites.—Five specimens examined. All contain sodium, potassium, silver, manganese, and apparently rubidium; 4 contain calcium; 4, lead; 3, copper; 3, nickel; 1, gallium; 1, thallium; and 1, chromium.

Red hæmatites.—Eighteen specimens examined. All contain sodium and potassium; 17 contain copper; 14, manganese; 13, silver; 12, lead; 12, calcium; 3 contain gallium; 3, indium; 3, nickel; 2, chromium; 1, rubidium; and 1, thallium.

Magnetites.—Seven specimens examined. All contain sodium, potassium, copper, silver, calcium, gallium, lead, and manganese. Four appear to contain rubidium; 2, nickel; and 1 contains indium.

Siderites.—Five specimens examined. All contain sodium, potassium, copper, silver, calcium, indium and manganese; 3 contain lead; 1 contains rubidium; 1, gallium; 1, cobalt; 1, nickel; and 1 bismuth.

Aluminous minerals, such as bauxites.—Seventeen specimens. All contain sodium, potassium, copper, calcium, and iron; 16 contain gallium; 15, chromium; 13, nickel; 12, manganese; 9, silver; 3, lead, and 2, rubidium.

Manganese ores and minerals.—Eleven specimens examined. All contain sodium, potassium, copper, calcium, and iron; 10 contain silver; 5, rubidium; and 5, nickel; 4, gallium; 4, lead; and 4, strontium; 2, barium; 1, indium; and 1, cobalt.

Blendes.—Fourteen specimens examined. All contain sodium, copper, silver, and iron; 13, potassium; 12, gallium; 12, lead; 10, silver; 10, manganese; 9, indium; 7, cadmium; 4, thallium; 2, nickel; and 1, chromium. The zinc was observed in only 8 specimens, the spectrum being hidden by other lines.

Nickel and Cobalt ores.—Nine specimens examined. All contain sodium, potassium, copper, calcium, iron, and nickel; 6 contain cobalt; 6, lead; 4, chromium; 3, silver; 1, barium; and 1, strontium.

Tin ores.—Five specimens examined. All contain sodium, indium, and iron; 4 contain potassium; 3, copper; 3, calcium; 3, lead; 2, silver; and 2, manganese.

Galenas.—Eight specimens. All contain sodium, potassium, copper, silver, and iron; 4 contain manganese; and 3, calcium.

Pyrites.—Thirteen specimens. All contain sodium, potassium, copper, silver, calcium, and iron; 11 contain lead; 10, manganese; 5, indium; 5, thallium; 5, nickel; and 1, gallium.

Out of 168 ores and minerals examined, gallium occurs in 68; indium in 30; and thallium in 17. Rubidium occurs probably in 70, but unquestionably in 13. All the carbonates of iron and all the tin ores, without exception, contain indium. With one single exception, all the bauxites contain gallium.

Silver, copper, calcium, potassium, and sodium are very widely disseminated through all ores and minerals.

The authors draw deductions as to the formation of beds and lodes of ore from the following facts, which they claim to have established. First, that certain groups of ores and minerals are pervaded by small quantities of the same metals as common impurities. Secondly, the rare metals, more particularly rubidium, gallium, indium, and thallium, are associated with the same groups of minerals, and also with allied groups.

It is easy to trace the association of similarly constituted compounds to their connection with elements related to each other, as determined by the periodic system of classification. These compounds have certain properties in common, distinctive of the groups of elements and compounds to which they belong; hence in a given course of chemical changes, similar compounds are formed and thrown together by precipitation or otherwise. All the minerals mentioned have undoubtedly had an aqueous origin.

The presence of the alkali metals in all the specimens, but in variable proportions, has a special significance.

In the analysis of many different precipitates, obtained both in neutral and even strongly acid solutions, the alkali metals have been found in combination with the precipitated substance. It has long been known that manganese, aluminium, and iron in the state of hydroxides, combine with more or less of the alkalis, but in a great measure such combinations have been disregarded.

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Pharmaceutical Society of Great Britain, The Calendar of the, 1897. Pp. 507. London. From the Society.

Thorp, Frank Hall. Inorganic Chemical Preparations. Pp. iv. + 236. Boston, U.S.A. 1896. From the Publishers.

Pamphlets.

Gilchrist, Percy C. Paper on the Bertrand-Thiel Process of Making Steel. Parts I. to VI. London 1896. From the Author.

Head, Jeremiah. The Manganese Ore Deposits of Northern Spain. London 1896. (Reprinted from the Journal of the Iron and Steel Institute.) From the Author.

Head, Jeremiah. American and English Methods of Manufacturing Steel Plates. (Reprinted from the Proceedings of the Institution of Civil Engineers.) London 1896. From the Author.

Mackenzie, W. C., and Foaden G. P. Manures in Egypt and Soil Exhaustion. Cairo 1896. From the Authors.

Newman, K. La Unifikazion de las Medidas. Valparaiso, 1897. From the Author.

ANNIVERSARY MEETING.

The Anniversary Meeting will be held on Wednesday, March 31st, at 3 o'clock in the afternoon.

ANNIVERSARY DINNER.

It has been arranged that the Fellows of the Society and their friends shall dine together at the Criterion Restaurant on Wednesday, March 31st, at 6.30 for 7 p.m.

At the next meeting, on Thursday, February 4th, the following papers will be received. The authors of those marked with an asterisk have signified their intention of being present.

* "The Oxidation of Nitrogen." By Lord Rayleigh.

* "An Improved Apparatus for Steam Distillation." By F. E. Matthews, Ph.D.

* "Researches in the Stilbene Series I." By J. J. Sudborough, Ph.D.

* "Di-ortho Substituted Benzoic Acids III. Hydrolysis of Substituted Benzamides." By J. J. Sudborough, Ph.D., P. G. Jackson and L. L. Lloyd.

RICHARD CLAY AND SONS, LIMITED, LONDON AND BUNGAY.

Issued 16/2/1897.

PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

EDITED BY THE SECRETARIES.

No. 174. Session 1896–7.

February 4th, 1897. Mr. A. G. Vernon Harcourt, President, in the Chair.

Mr. H. L. Bowman was formally admitted a Fellow of the Society.

Certificates were read for the first time in favour of Messrs. John Owen Alexander, 11, Avenue Road, South Norwood Park, S.E.; John B. Ashworth, 16, Ducie Street, Prince's Park, Liverpool; John Barclay, B.Sc., Avenue Cottage, near Bromsgrove, Worcestershire; Frank Bastow, B.Sc., 1, Braithwaite, Keighley; William Dillon, 7, Laurel Place, Chapel Lane, Armley, Lancashire; E. G. Guest, M.A., The Grammar School, Kirkham, Lancashire; T. Hartley, Gatwell Street, Bruton, Somerset; John Holmes, Crewe Villa, Putney Bridge Road, S.W.; O. C. Johnson, 52, Thayer Street, Ann Arbor, Michigan, U.S.A.; H. King, B.Sc., 4, North Street, Scarborough; H. M. Lloyd, 28, Victoria Street, Merthyr; R. N. Lyne, Government Offices, Zanzibar; C. H. Parker, Manor House, Tettenhall, Wolverhampton; S. Pollitt, B.Sc., 19, Paulton Square, Chelsea, S.W.; M. Wilderman, Ph.D., Davy Faraday Laboratory, Albemarle Street, W.

Of the following Papers, those marked * were read.

***10. "Observations upon the oxidation of nitrogen gas." By Lord Rayleigh, F.R.S.**

On the basis of Davy's assertion that the dissolved nitrogen of water is oxidised during electrolysis, various attempts were made; but they led to no useful result, even leaving it doubtful whether Davy's facts are correct.

The influence of pressure upon the oxidation of nitrogen by the electric flame was next examined. It appeared that, while in a small vessel the effect of increased pressure was favourable, but little advantage resulted when the vessel was large enough to give the maximum

effect at a given pressure. The pressures compared were two atmospheres, one atmosphere, and half an atmosphere.

The remainder of the paper is devoted to a detailed description of a large scale apparatus (shown working) in which 21 litres of mixed gases enter into combination per hour, at an expenditure of about 1 horse-power.

Discussion.

Professor Armstrong, referring to Lord Rayleigh's remark as to the importance of the platinum electrodes being red-hot, enquired whether there was any evidence that the platinum played a special part in the process.

Professor Ramsay suggested, as an explanation of the better results obtained when a large vessel was employed, that nitric oxide was the first product, and that this subsequently combined with oxygen to form the peroxide.

The President considered it probable that some of the oxide of nitrogen first formed was subsequently decomposed by the heat of the flame itself, and that the large vessel, by presenting a large surface of alkaline liquid, favoured the rapid absorption of the oxide of nitrogen, and thus less was decomposed than would be the case in a smaller vessel, where the rate of absorption was smaller. He enquired with what proportion of nitrogen to oxygen combustion occurred most rapidly.

Professor M'Leod remarked that he had made an experiment in the manner originally suggested by Cavendish, and had found that nitrite as well as nitrate was formed.

Lord Rayleigh, in reply, said that the larger vessel apparently led to better results by increasing the facilities for absorption. He did not consider that the platinum played any special part in the process. The action seemed most rapid when the proportion of air to oxygen was as about 5 to 6, which corresponds with two of nitrogen to three of oxygen. He believed that both nitrite and nitrate were formed. The apparatus shown was suitable for the preliminary concentration, but not for the final purification of argon.

***11. "On some apparatus for steam-distillation." By F. E. Matthews, Ph.D.**

In this paper several forms of apparatus for automatically steam-distilling substances are described.

Some solids of high melting point may be separated by boiling the substance mixed with water in a flask fitted with a reflux condenser, the solid substance adheres to the inside of the condenser, whence it can be removed from time to time.

For liquids heavier than water, the flask in which the mixture is

boiled is connected with the side tube of an ordinary distilling-flask; this distilling-flask, filled with water up to the side-tube, serves as the receiver. Into the neck of the receiver and passing below the surface of the water, a bent Liebig's condenser is fitted which has the peculiarity of having a hole made in it a short distance above the level of the water in the receiver. On boiling the mixture in the flask, the vapours pass up the side-tube of the receiver into the upper portion of its neck and thence through the hole into the receiver when condensation takes place. The condensed liquids run down the condenser to the water-level in the receiver, where a drop of the heavy fluid sufficiently large to sink is formed from time to time. The condensed liquids displace their own volume of water, which flows from the receiver through the side tube back again to the boiling-flask. In all cases in which vapour is passing in one direction in a tube, and water in the other, the advantage of perforating the tube near its lower end is pointed out.

For liquids lighter than water, the apparatus consists of the boiling-flask, which is an ordinary distilling flask; this is connected by the upper opening to an upright tube furnished with a T-piece. The top of the upright tube is connected to the condenser, the lower end dips two or three inches into a Woulfe's bottle, containing water in sufficient quantity, which serves as the receiver. Through another neck of the Woulfe's bottle, a second tube passes from the bottom of the bottle and is connected to the side-tube of the boiling-flask. The mixed vapours pass from the boiling-flask into the upright T-tube, thence into the condenser; there becoming condensed, they fall down into the T-tube, producing a column of liquid which forces water from the bottom of the receiver back into the boiling-flask through its side-tube.

A modification of this apparatus dispenses with the necessity of having an india-rubber connection exposed to the hot vapour. In this modification the boiling flask is an ordinary plain flask. This is connected to the condenser by a side-tube blown on to the upright tube. The water returns to the boiling-flask through another T-tube, blown on to the side-tube of the upright tube. For conveniently emptying the receiver without dismantling the apparatus, a separating-funnel with two necks may replace the Woulfe's bottle of the previous apparatus.

Many liquids bump badly when boiled with water; this can generally be got over by introducing a zinc platinum couple into the boiling-flask. The temperature of the water in the boiling-flask may be raised by dissolving suitable substances such as sulphuric acid or calcic chloride in it, or liquids of higher boiling point may be used.

***12. "Researches in the Stilbene Series. I." By John J. Sudborough, Ph.D.**

The author has obtained benzil as one of the products of the action of zinc dust and acetic acid on benzoïn; if the action is con-

tinued the benzil disappears and the chief product is deoxybenzoïn. The formation of an oxidation product of benzoïn by the action on it of zinc dust and acetic acid appeared so remarkable that the author has studied the action of acetic acid alone on benzoïn, and he finds that small quantities of benzil are formed if benzoïn is heated with six times its weight of glacial acetic acid on the water bath for eight—nine hours.

By the action of phosphorus pentachloride on deoxybenzoïn a solid chlorstilbene has been obtained, which differs from Zinin's oily compound. It melts at 45°, yields a dibromide and a dichloride, also with nitrous fumes two compounds probably represented by the formulæ $Ph\cdot CHNO_2\cdot CClNO_2\cdot Ph$ (m. p. 128°) and $Ph\cdot C(NO_2):C(NO_2)\cdot Ph$ (yellow prisms m. p. 104—105°).

An oily compound can be obtained by the action of phosphorus pentachloride on deoxybenzoïn at low temperatures. The oil contains the same amount of chlorine as solid chlorstilbene.

Methyldeoxybenzoïn and ethyldeoxybenzoïn on treatment with phosphorus pentachloride can be made to yield both oily and crystalline compounds, analysis of which points to their being methyl- and ethylchlorstilbenes. Solid methylchlorstilbene melts at 124°, and the corresponding ethyl compound at 60°. The dichlorides and dibromides are also described. The question as to the nature of the oily compounds has not been settled; the author describes a method by which he proposes to determine whether they are merely slightly impure forms of the solid compound, true stereo-isomerides, or structurally isomeric with the solid compounds.

***13. "Diortho-substituted benzoic acids. III. Hydrolysis of substituted benzamides." By John J. Sudborough, Ph.D., Percy G. Jackson, and Lorenzo L. Lloyd.**

In order to determine whether diortho-substituted benzamides exhibit the same remarkable degree of stability towards hydrolysing agents as characterises the diortho-benzoyl chlorides (Trans., 1895, 67, 587) and ethereal salts, the authors have investigated the following compounds.

Ortho-, meta-, and para-brombenzamide; 2 : 4-, 2 : 6- and 3 : 5-dibrombenzamide; 2 : 4 : 6- and 3 : 4 : 5-tribrombenzamide; 2 : 4 : 6-trichlorbenzamide; 2 : 4 : 6-trimethylbenzamide (mesitylformamide) and mesitylacetamide, $C_6H_2Me_3\cdot CH_2\cdot CONH_2$. Of the three mono-substituted brombenzamides the ortho-compound proves to be somewhat more stable in the presence of boiling (30 per cent.) sulphuric acid than the meta- and para-compounds. This agrees with the properties of the corresponding methylic monobrombenzoates and of the monobrombenzoyl chlorides.

Of the three dibromamides the 2 : 6- or di-ortho-substituted compound proves to be the one most difficult to hydrolyse by means of

75 per cent. sulphuric acid, and again of the two tribromamides the 2 : 4 : 6- or symmetrically substituted amide is much more stable than the isomeric 3 : 4 : 5-tribrombenzamide. 2 : 4 : 6-trichlorbenzamide although not hydrolysed so readily as 2 : 4- and 3 : 5-dibrom- and 3 : 4 : 5-tribrombenzamide is less stable than the corresponding 2 : 4 : 6-tribrom-compound.

The methyl derivatives could not be investigated as regards their hydrolysis with 75 per cent. sulphuric acid, as they are charred and decomposed by this means. Towards 30 per cent. sulphuric acid, the mesitylformamide is much more stable than the corresponding acetamide.

In the course of this investigation the following new compounds have been obtained :—3 : 5-Dibrombenzamide, m. p. 187°; 2 : 4 : 6-tribrombenzonitrile, m. p. 127°; 2 : 4 : 6-tribrombenzamide m. p. 193—194°; 3 : 4 : 5-tribrombenzamide, m. p. 199°; 2 : 4 : 6-trichlorbenzonitrile, m. p. 75°; 2 : 4 : 6-trichlorbenzamide, m. p. 177°; mesitylformamide, m. p. 105°; mesitylacetamide, m. p. 210°.

***14. "Conversion of camphoroxime into methylcamphorimine and camphenylnitramine." By M. O. Forster, Ph.D.**

Further investigation of the base obtained on heating camphoroxime in sealed tubes with methylic iodide has proved it to be the methyl-derivative of Tiemann's camphorimine; it therefore has the formula $C_8H_{14}<\begin{matrix}CH_2\\|\\C{:}N\cdot Me\end{matrix}$, and not, as appeared probable from the preliminary examination (Proc., 1895, 11, 145), the formula, $C_{12}H_{19}N$. This is shown by its behaviour towards concentrated hydrochloric acid at 200°, giving rise to camphor and methylamine.

Methylcamphorimine hydrochloride and *methiodide* melt at 270° and 231—232°, respectively; the *perbromide* has also been prepared.

The action of dilute nitric acid on camphoroxime, if interrupted after a few minutes, gives rise to *camphenylnitramine*, which is also formed when a solution of the oxime in chloroform is treated with nitrogen peroxide.

An acid solution of potassium permanganate converts camphoroxime into an unstable nitroso-derivative, which separates from the liquid as a sticky, green mass; when preserved in the desiccator the substance deliquesces, and loses its green colour, the yellow residue yielding camphor when distilled in an atmosphere of steam.

15. "Note on Wechsler's method for the separation of fatty acids." By Arthur W. Crossley.

Wechsler (*Monatsh.*, 1893, 14, 462) has described a method for the separation of fatty acids, the principle of which method is contained in the following statement.

If to a mixture of two fatty acids four-fifths of the caustic soda necessary to neutralise them be added, and the whole steam-distilled, the distillate contains the pure higher-boiling acid. From the residue of the distillation a further three-fifths of the acids are set free by addition of sulphuric acid, and the whole distilled in steam. Finally, the remaining fifth of the acids is set free, and in this case the distillate contains the lower boiling acid in a pure condition.

The purity of the acids contained in the various distillates was proved by converting them into silver salts and subsequent analysis of these salts.

After trying this method of separation, with very unsatisfactory results, on a mixture of fatty acids obtained in a research on which Professor Perkin and the author have been engaged for some time past, it was thought advisable to test some of Wechsler's experimental data.

Accordingly, Wechsler's experiments have been carefully repeated and results obtained which do not agree with that author's.

As Wechsler always worked with equimolecular proportions of fatty acids, the result of some experiments are recorded in which varying proportions of fatty acids were employed. In every case, the results were unsatisfactory, for even when using three molecules of the lower to one of the higher boiling acid, the former was not obtained pure in the last distillate, and the first distillate contained a decided mixture of the two acids.

It is therefore to be concluded that Wechsler's method does not give such good results as its author suggests, nor can it in any way be looked upon as a satisfactory method for separating mixtures of fatty acids.

16. "On the crystalline structure of gold and platinum nuggets and gold ingots." By A. Liversidge, LL.D., F.R.S.

In view of the theory that gold nuggets are built up of concentric layers deposited round a central nucleus, the author has examined a large number of specimens from various sources. The nuggets were ground down, or sliced through, to obtain sections, which were polished and etched by suitable solvents. They all possess a well-marked crystalline structure, and usually enclose foreign substances. The crystalline structure is not incompatible with an aqueous origin; and the author suggests that the gold has been slowly deposited from solution, either at ordinary or at high temperatures: the nuggets being more or less rolled masses of gold which have been set free from disintegrated veins.

17. "On the presence of gold in natural saline deposits and marine plants." By A. Liversidge, LL.D., F.R.S.

The author gives a preliminary account of the results of the examination for gold of rock salt, sylvine, and other similar saline

deposits, bittern, sea-weed, kelp, oyster shells, &c. The process of determination used was to add from 0·5 to 5 grams of ferrous sulphate to the unfiltered solution of 100 to 1000 grams of the salt in water. The resulting precipitate was then scorified with lead and cupelled. The natural salts contained from 1 to 2 grains of gold per ton, whilst kelp and bittern furnished in some cases as much as from 14 to 20 grains.

ADDITIONS TO THE LIBRARY.

I. *By Purchase.*

Berthelot, M. Science et Morale. Pp. xii+518. Paris 1897.

Hoff, J. H. van't. Vorlesungen über Bildung und Spaltung von Doppelsalzen. Pp. iv+95. Mit 54 figuren im Text. Leipzig 1897.

Venables, F. P. The Development of the Periodic Law. Pp. viii+321. Easton, U.S.A. 1896.

II. *Donations.*

Cannizzaro, S. Scritti intorno alla Teoria Molecolare ed Atomica ed alla notazione chimica di. Pubblicati nel 70° Anniversario della sua nascita (13 Luglio 1896). Pp. 387, with portrait. Palermo 1896.
From Prof. S. Cannizzaro.

Davy, Sir Humphry. Six Discourses delivered before the Royal Society at their Anniversary Meetings on the award of the Royal and Copley Medals, preceded by an Address to the Society on the Progress and Prospects of Science. Pp. xii+148. London 1827.
From the Librarian.

Fink, E. Précis d'Analyse Chimique, Première Partie, Analyse Qualitative. Pp. 190. Deuxième Partie, Analyse Quantitative. Pp. 312. Paris 1896. From the Publishers.

Haller, A. et Muller, P.-Th. Traité Élémentaire de Chimie. Chimie Minérale. Pp. 336. Chimie Organique. Pp. 205. Paris 1896.
From the Publishers.

Moscow, Memoirs of the Imperial University of. Physico-Mathematical Series and Natural Science Series. Vols. I—XII. 1880—96.
From S. G. Rosenblum.

Pamphlets.

British Association for the Advancement of Science. Toronto Meeting, 1897. Preliminary Programme, with Maps and Illustrations. Toronto 1896. From the Association.

RESEARCH FUND.

Mr. J. J. Tustin has made a donation of One Thousand Guineas to the Research Fund of the Society.

PASTEUR MEMORIAL LECTURE.

The Pasteur Memorial Lecture will be delivered by Professor Percy Frankland, Ph.D., F.R.S., at an extra meeting of the Society on Thursday, March 25th, at 8 p.m.

ANNIVERSARY MEETING.

The Anniversary Meeting will be held on Wednesday, March 31st, at 3 o'clock in the afternoon.

ANNIVERSARY DINNER.

It has been arranged that the Fellows of the Society and their friends shall dine together at the Criterion Restaurant on Wednesday, March 31st, at 7 p.m.

At the next meeting, on February 18th, the following papers will be received. The authors of those marked with an asterisk have announced their intention of being present.

* "The oxidation of sulphurous acid by potassium permanganate." By T. S. Dymond and F. Hughes.

"Sodamide, and some of its substitution derivatives." By A. W. Titherley, M.Sc., Ph.D.

"Rubidamide." By A. W. Titherley, M.Sc., Ph.D.

"Dissociation pressure of alkyl ammonium hydrosulphides." By J. Walker, D.Sc., and J. S. Lumsden, Ph.D.

"On the spectrographic analysis of some commercial samples of metals, of chemical preparations and minerals from the Stassfurth potash beds." By W. N. Hartley, F.R.S., and H. Ramage.

"Supposed condensation of benzil with ethyl alcohol: A correction." By F. R. Japp, LL.D., F.R.S.

* "The viscosity of mixtures of miscible liquids." By T. E. Thorpe, LL.D., F.R.S., and J. W. Rodger.

CERTIFICATES OF CANDIDATES FOR ELECTION AT THE NEXT BALLOT.

N.B.—The names of those who sign from "General Knowledge" are printed in *italics*.

The following Candidates will be balloted for on March 4th.

Alexander, John Owen,

11, Avenue Road, South Norwood Park, S.E.

Analytical Chemist. Six years Assistant to the late Dr. Wallace, Glasgow. Six years Chemist in Demerara. Have done special Sugar reporting work in Louisiana, Brazil, France, Belgium, Germany, French West Indies, Antigua. Now managing Messrs. Cannon & Newton's Analytical Laboratory, 39, Mincing Lane, E.C.

Frank L. Teed. B. E. R. Newlands.
D. A. Louis. John A. R. Newlands.
William Newton.

Arbuckle, William,

34, Moore Street, Cadogan Square, S.W.

Assistant in the Davy-Faraday Research Laboratory of the Royal Institution. Four years Assistant in the Chemical Laboratory of the Heriot-Watt College, Edinburgh, under Professors W. H. Perkin, jun., and J. Gibson. Eighteen months as Student in R. R. Tatlock's (City Analyst) Laboratory, Glasgow.

W. H. Perkin, jun. James Dewar.
Alexander Scott. Robert. N. Lennox.
John W. Heath.

Ashworth, John B.,

16, Ducie Street, Prince's Park, Liverpool.

Analytical Chemist. Assistant for 8 years to Mr. Alfred Smetham. Conducted, conjointly with Mr. Smetham, investigations into the Chemistry of Cheshire Cheese-making on behalf of the Board of Agriculture.

Alfred Smetham. Bernard Dyer.
J. Augustus Voelcker. *Charles S. Cassal.*
Otto Hehner.

Barclay, John,

Avenue Cottage, near Bromsgrove, Worcestershire.

Member of firm of Southall Bros. and Barclay, Birmingham, Manufacturing Chemists. (1888) B.Sc., London University, 3rd Class Honours in Chemistry. Four years Lecturer in Materia Medica at Mason College. Associate of Mason College. Pharmaceutical Chemist. Writer of several papers (Materia Medica, Pharmaceutical Chemistry), published in *Pharmaceutical Journal* Author of 5th edition, Southall's Materia Medica, 1896.

William A. Tilden.	John Attfield.
Thomas Turner.	W. W. J. Nicol.
J. J. Sudborough.	Arthur J. Cooper.

Bastow, Frank,

1, Braithwaite, Keighley, Yorkshire.

Head-Master, Science Department of the Technical Schools, Salt Schools, Shipley. For four years a Student at the Royal College of Science, South Kensington, attending the courses in Chemistry, Physics, Botany, Biology, Geology, and Mechanics. Bachelor of Science and Bachelor of Arts, London University. For ten years past a Teacher of Theoretical and Practical Chemistry, having prepared students for all stages of the Science and Art Department's Examinations.

James Spencer.	Thomas J. Roberts.
George W. Slatter.	*Thorp Whitaker.*
Walter M. Gardner.	*C. Rawson.*

A. Rée.

Brown, James Herbert,

Dallas Place, Lancaster.

Assistant Manager at the Corporation Gas Works, Lancaster. Educated at the Dewsbury Wheelwright Grammar School under A. E. Holme, Esq., M.A. (Oxon.). Obtained a Two Years' Akeroyd Science Scholarship to the Yorkshire College, Leeds. Studied Chemistry under Professor Smithells and Mr. Ingle. After which I was employed by J. Brown & Co., Manufacturing Chemists, Dewsbury, as Public Analyst, and am at present Assistant Manager to Charles Armitage, Esq., A.M.I.C.E., Engineer and Manager at the Corporation Gas Works, Lancaster.

Chas. Armitage.	A. E. Holme.
Arthur Smithells.	Herbert Ingle.
Joseph Brown.	*R. L. Barnes.*

Cartmell, Alfred,

Alexandra Road, and The Laboratory, Burton-on-Trent.

Analytical Chemist and Consulting Brewer. Analyst to the Tutbury and Repton Rural District Council. Ten years Chemical Assistant

to the late Rowlandson Cartmell, F.C.S., and also Successor to since 1888.

Adrian J. Brown.	Walter Odling.
C. O'Sullivan.	G. Harris Morris.
Horace T. Brown.	*William W. Butler.*

John Spiller.

Chikashigé, Masumi,
Kumamoto, Japan.

Professor of Chemistry. B.Sc., Imperial University, Japan. Five years as Student of Chemistry in the Laboratories of the University. Author of papers on "Mercury Perchlorates" and "The Atomic Weight of Japanese Tellurium" in the *Chemical Society's Journal*; and of two notes in the *Chemical News*.

Edward Divers.	Jōji Sakurai.
Toyokichi Takamatsu.	Hikorokuró Yoshida.
Tamemasa Haga.	Michitada Kawakita.

Cholerton, Alfred Foster,
Lyndum House, Lincoln Street, Leicester.

Manufacturing Chemist. Engaged over 20 years in Manufacturing Chemistry with Practical Laboratory Work. Formerly Student at University College, Nottingham. Partner in the firm of A. de St. Dalmas & Co., Leicester.

Frank Clowes.	Geo. Ward.
Thomas Fairley.	S. F. Burford.
Lewis Ough.	*J. J. Sudborough.*

Godfrey Melland.

Creasey, Clarence Hamilton,
78, Baggeholme Road, Lincoln.

Lecturer on Chemistry and Physics, School of Science, Lincoln. Originally trained as an Engineer, spending five years at R. Howesly & Son's, Spittlegate Ironworks. Gave up Engineering for Chemistry, and spent two years at Royal College of Science, London, studying Chemistry and Physics 1894—6. Appointed to present post September, 1896. Desirous of keeping abreast of recent Chemical discoveries.

William A. Tilden.	W. Palmer Wynne.
M. O. Forster.	J. S. S. Brame.

A. E. Tutton.

Crowther, James,
West Field, Lightcliffe, Halifax.

Head-Master Technical School, Halifax. Two years Assistant Lecturer in Chemistry at the Manchester Technical School. Bachelor

of Science, London. Chemistry one of the subjects for Final Examination. Honours, Theory, Science and Art Department.

Gibson Dyson. John Allan.
Jas. Grant.] *Ernest Bentz.*
William L. Hiepe.

Davis, William Alfred,
108, Gordon Road, Peckham, S.E.

Chemist to Messrs. S. Courtauld & Co., Crape Manufacturers, Braintree, Essex. Associate of the City and Guilds Institute. Author of "3'-Bromo-betanaphthol" (jointly with Dr. Armstrong), and of "Derivatives of Nitro-β-naphthols," and "Morphotropic Relations of Betanaphthol Derivatives" (*Proceedings*, 1896, pp. 230—234).

Henry E. Armstrong. F. Stanley Kipping.
W. Palmer Wynne. William J. Pope.
Gerald T. Moody.

Diamond, William,
Pye Bridge, Alfreton.

Chemist, Pye Bridge Chemical Works, Derbyshire. Was Student, Chemical Laboratory University College, Nottingham, and now Assistant Manager under Kempson & Co., Chemical Works, Pye Bridge.

Frank Clowes. J. Bernard Coleman.
R. Lloyd Whiteley. J. J. Sudborough.
Godfrey Melland.

Dillon, William,
7, Laurel Place, Chapel Lane, Armley, Leeds.

Commercial Traveller. Evening Class Teacher in Leeds Technical School. Works Analyst. Eight years' training in Chemistry and other Sciences at the Leeds School of Science. Three years as Demonstrator. Lecturer on Oils and Fats at Leeds Technical School. Bronze Medallist and First Class Honours of City and Guilds of London Institute.

Thomas Fairley. B. A. Burrell.
S. J. Harris. F. W. Branson.
Geo. Ward.

Dodgson, John Wallis,
47, Hirwain Road, Aberdare, Glamorganshire.

Teacher of Science. For 4 years (1892—96) Demonstrator and Assistant Lecturer at University Extension College, Reading. B.Sc. London University (Chemistry, Physics, Pure Mathematics). At present Science Teacher, Aberdare Technical and Intermediate Schools. Joint author of paper, "Action of Strong Acids upon Metals when in

Contact with One Another," read before the Society by Mr. G. J. Burch, M.A., and published in the Society's *Proceedings*, May, 1894.

W. W. Fisher. Walter Palmer, B.Sc.
J. E. Marsh. J. A. Gardner.
V. H. Veley. *P. Elford.*

Dufty, Lawrence,
33, Broomhall Place, Sheffield.

Analytical Chemist. Assistant Evening Demonstrator in Metallurgical Laboratory, Sheffield Technical School. Last 7 years Senior Chemist at the Continental Steel Works, Attercliffe. Four years evening Student in Chemistry and Metallurgy, Sheffield Technical School. Associate of the School and Mappin Medallist for Metallurgy, Hadfield Medallist for Research Work in connection with Metallurgy. Sheffield Society of Engineers and Metallurgists. Paper on "The Determination of Silicon and Tungsten in Tungsten Steels," published in the above Society's *Journal*.

B. W. Winder. G. T. W. Newsholme.
Fredk. J. Merrils. Chas. Bradshaw.
Thos. Andrews.

Edwards, William Buckland,
5, Garlinge Road, Brondesbury, N.W.

Student. Student for three years in the Chemistry Department of the Central Technical College, and have been engaged during the present year in Research Work under Dr. Armstrong. Published a note with Dr. Kipping on Dimethylketohexamethylene in the *Proceedings*, No. 169.

Henry E. Armstrong. Gerald T. Moody.
F. Stanley Kipping. William J. Pope.
R. Berncastle.

Gibbons, Joseph Lake,
West Carlton Street, Blyth.

Principal of the Higher Grade Schools, Blyth, Northumberland (3 years). Late Senior Science Assistant, Gateshead Higher Grade Schools (9 years). Formerly Student-demonstrator in Science, Carmarthen Training College for Schoolmasters. Trained, Certificated (first in 1st Division) Teacher. College Exhibitioner. Lecturer in Science (Chemistry, Physics, Mathematics). Passed Science and Art Department's advanced examinations in Chemistry and Physics. Passed Chemistry, Physics, Mathematics Branch Second Arts Examination of Royal Uni-

versity, Dublin. Takes personal charge of the Science Department of the Blyth Higher Grade and Organised Science Schools.

Duncan T. Richards. William Fowler.
Charles Ranken. *P. Phillips Bedson.*
C. H. Corbett.

Gilbody, Alexander William,
Owens College, Manchester.

M.Sc. Victoria University, Ph.D. Munich. Four years as Student in Owens College Laboratories. B.Sc. with Honours in Chemistry, 1890. Two years at the University of Munich, 1891—1893. From October, 1895, has been researching with Professor Perkin at Owens College. Author of "Ueber die Einwirkung von Chloral auf Messeler Pyridinbasen," *Berichte*, xxvi.

Harold B. Dixon. W. H. Perkin, jun.
A. Harden. G. H. Bailey.
Jocelyn F. Thorpe. Bevan Lean.
E. Haworth.

Gough, Harold Walter,
73, Billing Road, Northampton.

Assistant Master, and Lecturer on Advanced Physiology and Botany, and Elementary Sound, Light, and Heat, at Northampton and County Technical School. Natural Sciences Tripos, Pt. I. Scholar of Derby School, and Exhibitioner of Emmanuel College, Cambridge. Four months in Mr. Archbutt's Laboratory at Derby. Science Master at Wolverly Grammar School; and also at King Edward VI. School, Chelmsford, with Chemistry Class under the Essex County Council.

R. Elliot Steel. W. J. Sell.
H. J. H. Fenton. L. Archbutt.
Thomas H. Easterfield.

Goulding, Ernest,
18, Mercers Road, Holloway, N.

Assistant Chemist, Scientific and Technical Department, Imperial Institute. Student in the School of the Pharmaceutical Society, 1892–93. Student in the Research Laboratory of the Pharmaceutical Society, 1893–96. Joint author with Professor W. R. Dunstan of the following:—"The Action of Methylic Iodide on Hydroxylamine" (*Proc.* C.S., 1894, 138); "The Hydriodides of Hydroxylamine" (*J.C.S.* 1896, 839).

Wyndham R. Dunstan. F. A. Abel.
Percy F. Frankland. Herbert McLeod.
D. Hamilton Jackson.

Guest, Edward Graham,

The Grammar School, Kirkham, Lancashire.

Science Master at Kirkham Grammar School. M.A. Corpus Christi College, Cambridge. Intermediate B. Sc. London (Final in Chemistry and Geology, 1896.) Four years Science Teaching as Master at Ruthin School and Kirkham Grammar School.

Robert Irvine.	Alex. Crum Brown.
W. S. Anderson.	Frank T. Addyman.
Stevenson Macadam.	*W. Ivison Macadam.*

Harley, Vaughan,

25, Harley Street, W.

Professor of Pathological Chemistry, University College, London. M.D., M.R.C.P. "Chemical Changes of Sugar in Organism," *Proc. Roy Soc.* v., 54, 1893. "Sugar as a Food in the Production of Muscular Work," *Proc. Roy Soc.*, 1894. "The Chemical Pathology of Uric Acid," *Brit. Med. Journal*, 1895. "Absorption of Fat," *Journal of Physiol.*," 1895; "Beitrage zur Phys. des Blutzuckers," *Arch. J. d. ges. Phys.* 1895, &c.

William Ramsay.	John Shields.
G. Carey Foster.	Morris W. Travers.

Edward C. Cyril Baly.

Hartley, Ernald George Justinian,

Wheaton Aston Hall, Stafford.

B.A. (Oxon.). First Class Honours in Final Chemistry examination. Still studying Chemistry in Christ Church Laboratory.

A. Vernon Harcourt.	D. H. Nagel,
J. E. Marsh.	P. Elford.

Berkeley.

Hartley, Thos.,

Patwell Street, Bruton, Somerset.

Schoolmaster. Studied Chemistry as Brown Scholar at the Yorkshire College, Victoria University, in 1888—89—90, subsequently engaged in school teaching, and at present Science Master in Sexey's Trade School, Bruton (Organised Science School).

Arthur Smithells.	Charles H. Bothamley.
Alfred E. Tutton.	Wm. A. Knight.
Herbert Ingle.	Hy. Ellison, jr.

Heppenstall, Charles,

Ferrybank, Arklow, Co. Wicklow.

Manager of Messrs. Kynoch's Explosives and Chemical Works, Arklow. Three years Manager and Chemist, Fortis Powder Works. Four years Assistant Chemist, Brown Bayly's Steel Works. Honours,

Certificates, and Medals, City and Guilds of London Institute in Iron and Steel Manufacture, and Fuel.

W. H. Greenwood.	A. T. Cocking.
C. R. C. Tichborne.	Harry Carter Draper.
Jno. Northing.	*J. Emerson Reynolds.*

Ernest Scott.

Holmes, John,

Crewe Villa, Putney Bridge Road, S.W.

Assistant, Government Laboratory, Somerset House. Student for 8 years at Giggleswick. Last 4 years mainly devoted to Science subjects. One year in Laboratory of Jas. Baynes, Public Analyst, Hull. Two years' Chemical Training at the Royal College of Science, South Kensington.

T. E. Thorpe.	R. Bannister.
C. Proctor.	William A. Tilden.

Chapman Jones.

Ibbotson, Fred,

9, Melbourn Road, Spring Vale, Sheffield.

Lecturer on Chemistry, the Technical Schools, Sheffield. Associate Royal College of Science, Dublin. Bachelor of Science (1st Division) London University. Formerly Teacher of Chemistry at the Central Higher Schools, Sheffield, from 1889—1895; at present Lecturer in Chemistry at Sheffield Technical Schools and engaged on Organic Research during spare time.

W. N. Hartley.	L. T. O'Shea.
George Young.	W. Carleton Williams.
W. E. Adeney.	Hugh Ramage.

Innes, William Ross,

Mason College, Birmingham.

Demonstrator of Chemistry. B.Sc. of Victoria University (Honours, Chemistry), Ph.D. Heidelberg, A.I.C. Joint author with Professor Auwers of the paper entitled "Über das kryoskopische verhalten substituierter Phenole in Naphtalin," *Zeitschr. für Phys. Chem.*, xviii., 4.

Percy F. Frankland.	C. F. Baker.
Walter G. McMillan.	John McCrae.

Charles A. Kohn.

Jerdan, David Smiles,

68, Union Street, Greenock.

Student. M.A., University of Glasgow, 1892. B.Sc., with First Class Honours in Chemistry, Victoria University, 1895. University Fellow in Chemistry of the Victoria University. Joint author of

papers published in the *Proceedings* of the Society on "The Direct Union of Carbon and Hydrogen." At present engaged in research under Prof. Victor Meyer, Heidelberg.

Harold B. Dixon. W. H. Perkin, jr.
A. Harden. G. H. Bailey.
Bevan Lean. E. Haworth.

Johnson, Harold,

5, Boulevard Clovis, Bruxelles.

Analytical Chemist, engaged in the Laboratory of the *Petit Journal du Brasseur*, Bruxelles. Late Pupil of Mr. Sidney Harvey, Public Analyst, South Eastern Laboratory (General Analytical Chemistry). Late Pupil of Dr. Henri van Lauer, in General Chemistry, Analysis of Yeasts and Preparation of Pure ditto, Study of Ferments (Bacteria) and Enzymes, Member of the Belgian Chemical Society; have contributed papers on "L'acidité du moût," "L'analyse commerciale des glucoses." Have presented to the Belgian Brewers' Association a paper on "The Effect of Permanganate of Potash on Organic Contamination and Bacteria in Waters." Have obtained the First Class Honours Certificate in Brewing, London City and Guilds.

Sidney Harvey. John Grove Johnson.
A. Boake. *G. Harris Morris.*
C. O'Sullivan.

Johnson, Otis C.,

52, Thayer Street, Ann Arbor, Mich., U.S.A.

Professor of Applied Chemistry in the University of Michigan. Joint author of "Qualitative Chemical Analysis" (Prescott and Johnson's). Contributor of papers upon subjects in Analytical Chemistry.

Albert B. Prescott. Thomas H. Norton.
John G. Spenzer. Bennett F. Davenport.
Joseph F. Geisler.

King, Herbert,

4, North Street, Scarborough.

Science Teacher. Studied at the Yorkshire College, Leeds. Bachelor of Science in the Honours School of Chemistry, Victoria University. Passed the examination for the Associateship of the Institute of Chemistry (July, 1896). Second Master of St. Martin's Grammar School, Lecturer in Chemistry under the Scarborough School Board.

Arthur Smithells. Julius B. Cohen.
Herbert Ingle. J. J. Hummel.
Henry R. Procter.

Lang, William Robert,

9, Crown Gardens, Glasgow, W.

Senior Assistant to Professor of Chemistry, University of Glasgow. B.Sc. (with special qualification in Chemistry), Glasgow. Has been an

Assistant here since 1889 and has had 7 years' experience as a Teacher of both Practical and Theoretical Chemistry, with Lectures, Tutorial Classes, and Laboratory instruction.

John Ferguson. — John Clark.
G. G. Henderson. — Stevenson Macadam.
W. Ivison Macadam. — J. T. Bottomley.
Edw. C. C. Stanford.

Lee, Theophilus Henry,
Hampden House, Phœnix Street, N.W.

Analytical Chemist and Assayer. Assistant Chemist in the employment of Messrs. Johnson, Matthey & Co., Limited, previously Assistant Chemist in the Netham Works of the United Alkali Co., Limited.

John S. Sellon. — G. Matthey, F.R.S.
Edward Matthey. — Ernest H. Cook.
Tho. Coomber. — F. R. Stephens.

Lloyd, Henry Morgan, F.R.M.S., A.P.S.
28, Victoria Street, Merthyr.

Chemist, Operative and Dispensing. Analytical work conducted chemically and microscopically. Operative Pharmaceutical Chemistry.

Robt. Hy. Owen. — H. S. Shorthouse.
A. W. Duncan. — *F. Harwood Lescher.*
M. Conroy. — *W. A. H. Naylor.*
Alfred Southall.

Lyne, Robert Nunez,
Government Offices, Zanzibar.

Resident Lecturer. Lecturer on Agriculture and Agricultural Chemistry. Lecturer under the Lincolnshire County Council. Late Student and Diploma of the Canterbury (New Zealand) Agricultural College.

John Wrightson, F.C.S. — William French, M.A., F.I.C.
Hudson Donaldson. — *J. H. Gladstone.*
John M. Thomson.

Martin, Charles Henry,
14, Aldred Street, Crescent, Salford.

Chemist and Assistant Manager Oil and Soap Works. My past and present work is Analytical and Manufacturing Chemistry.

George H. Hurst. — R. Stockdale.
G. W. Davies. — *Charles Dreyfus.*
David Watson.

North, Barker,
3, Manor Terrace, Felixstowe.

Army Science Tutor and Lecturer in Chemistry, Physics, and Geology. Author of a paper on "Gawalowski's Method of Estimating

Sulphuric Acid" (*Proc.*); joint author of a paper on "Diethyl Phosphorous Acid" (*Trans.*); joint author of "Introductory Lessons on Quantitative Analyses," and "Handbook of Quantitative Analysis."

T. E. Thorpe. Percy F. Frankland.
A. E. Tutton. George T. Holloway.
J. W. Rodger.

Parker, Charles Henry,
Manor House, Tettenhall, Wolverhampton.

Chemist. From 1886 I have been engaged—3 years in the Electrical and Chemical departments of Elwell-Parker, Limited, Wolverhampton; 1889—90, Student at Tettenhall College; 1890—1, Student at Owens College; 3 years in Chemical Laboratory at Electric Construction Company, Wolverhampton; and 18 months with Key Syndicate, Wednesfield, on Chemical, Electro-chemical, and other Research work.

E. W. T. Jones. Chas. A. MacMunn.
Edward Bevan. Harold B. Dixon.
G H. Bailey *W. H. Perkin, jun.*

Pollitt, Samuel, B.Sc.,
19, Paulton Square, Chelsea, S.W.

Science Master in the Brompton Higher Grade and Organised Science School, S.W. First Division Final B.Sc. Examination Victoria University; First Class Honours Practical (Inorganic), and Second Class Honours Practical Organic, Science and Art Department; 3 years Student at Owens College, Manchester; 2 years Chemistry Master, King's Lynn Technical School.

H. B. Dixon. W. H. Perkin, jun.
G. H. Bailey. E. Haworth.
W. H. Bentley. Arthur Harden.
Bevan Lean.

Pullar, Herbert Spindler,
Rosebank, Perth, N.B.

Dyer. Student at Edinburgh University under Professor Crum Brown. Student at Yorkshire College, Leeds. Dyeing under Professor Hummel. Chemistry under Professor Smithells.

J. J. Hummel. A. G. Perkin.
Arthur Smithells. Rufus D. Pullar.
Geo. Ward.

Ralston, William,

337, Cathcart Road, Glasgow.

Chemist. B.Sc. (Lond.), A.I.C., Assistant to (late) Professor Dittmar, F.R.S. (L. & E.), LL.D., from 1886 to 1892. Assistant to Professor Henderson, M.A., D.Sc. F.I.C., from 1892 till the present.

G. G. Henderson.	A. Humboldt Sexton.
Thomas Gray.	Matthew A. Parker.
James Robson.	*Edmund J. Mills.*

Remington, John Stewart, M.R.A.C.,

Dromore, Milverton, Leamington.

Student. Formerly Student in Chemical Laboratory, Mason College of Science, Birmingham, from May, 1892, till July, 1894. Student and Member of the Royal Agricultural College, Cirencester, from September, 1894, to present time. Passed Honours, Diploma of Membership Christmas, 1896.

Edward Kinch.	Cecil Cooke Duncan.
Robt. Chas. Marchant.	William A. Tilden.

J. W. James.

Rosling, Edward,

Melbourne, Chelmsford.

Farmer and Landowner. Student of Royal College of Chemistry under the late Dr. Hofmann. Joint author with Dr. Bernard Dyer, of numerous reports on Field Experiments carried out for the Essex Agricultural Society. Interested chiefly in Agricultural Chemistry.

Bernard Dyer.	J. Augustus Voelcker.
Alfred Smetham.	John Spiller.
Charles E. Cassal.	*Otto Hehner.*

Southerden, Frank,

75, Barry Road, Dulwich, S.E.

Chemist to the Steel Brand Cement Factories. Have passed through the full Chemical course at Finsbury Technical College, and have the College Certificate. Worked for 8 months with Professor Meldola in his Research Laboratory on Constitution of Azo-compounds. For 3 years Chemist at Cement Works. An Associate of the Institute of Chemistry.

R. Meldola.	Geo. W. MacDonald.
E. S. Hanes.	M. O. Forster.

Julian L. Baker.

Stainer, William James, B.A., London,

3, Havelock Road, Stanford Avenue, Brighton.

Science Teacher (Chemistry and Mathematics principally). Author of *Synopsis of Advanced Chemistry* (published by Hughes & Co., 1*s.* 6*d.*)

Author of *Practical Chemistry Tables* (Stage E, South Kensington Syllabus). Second Master and Lecturer in Chemistry (up to Stage Advanced Theoretical and Practical, Inorganic, of South Kensington, Syllabus) to the Organised Science School (Brighton). Science Teacher to the Pupil Teacher Classes (Brighton) and to the Steyning (Sussex) Technical Education Committee (Sussex County Council).

William Briggs (M.A., LL.M.). William Jago.
R. L. Taylor. *Chapman Jones.*
Henry R. Redman. *E. J. Cox.*

Stevens, Henry Potter,

14, Lower Sloane Street, Chelsea.

Student. B.A. (Oxon.). Scholar of St. John's College, Oxford. 1st Class Honours, School of Natural Science, 1896 (in Chemistry).

W. J. Russell. F. D. Chattaway.
P. Elford. W. W. Fisher.

A. Vernon Harcourt.

Sumner, Leonard,

Butt Hill, Prestwich, near Manchester.

Assistant Manager of the Broughton Copper Works, Manchester. London University Matriculation (Honours), 1887. Articled Pupil in the Engineering Works of W. Muir and Co. (Manchester), 1887–90. Student in Owens College, 1890–93. B.Sc. (Victoria—Honours, Engineering) and Associate of Owens College, 1893. Student City and Guilds Central Technical College, Session 1893–4, and obtained Certificate in Electricity and Chemistry. Worked for nine months in the Chemical Laboratory of the Broughton Copper Co., 1894–5. Studied Metallurgy, under Prof. Roberts Austen, at the Royal School of Mines, Session 1895–6, and passed the final examination in the First Class.

W. C. Roberts Austen W. Gowland.
Henry C. Jenkins. David Watson.

G. FitzBrown.

Thompson, Harry,

Walton House, West Parade, Anlaby Road, Hull.

Analyst. 1892–5, Winter Sessions, Science and Art Classes; Teacher, G. Carr Robinson, F.R.S.E., F.I.C., F.C.S. September, 1895, July, 1896, Assistant to Dr. A. Röhrig, 20, Linden St., Leipzig. 1896, April to July, Leipzig University, Chemical Study. July to October, II. Assistant, Königliche Landwirthschaftliche Versuchsstation, Rufach, Elsass-Loth. Direktor, Prof. D. M. Barth. November, Analyst to the Black Point Syndicate, Limited, in Milo, Greece.

G. Carr Robinson. M. D. Penney.
Jas. Baynes. John Caley.

Fred. E. Johnson.

Turnbull, Andrew,

Daldowie, Broomhouse, near Glasgow.

Private Research Assistant to Prof. P. F. Frankland. Student at Glasgow and West of Scotland College, 1890–3. Assistant in Chemical Dept., 1893–4. Student at Heidelberg University, 1894–6. Graduated at Heidelberg (Chemistry, Physics, and Botany), 1896. Research: "Ueber Benzolazo-tetrahydro-α-Naphthol und seine Derivate."

Percy F. Frankland. — Charles Frederic Baker.
Walter G. McMillan. — G. G. Henderson.
James Robson. — Matthew A. Parker.
A. Humboldt Sexton.

Turner, Basil William,

C/o Henry Turner, Collins Street, Annandale, Sydney, New South Wales.

Assayer and Metallurgist. Associate of the Royal School of Mines, London, in the division of Metallurgy. Have pursued a course of study in Theoretical and Practical Chemistry at the Sydney University, N.S.W., and also at the Royal College of Science, London.

Chapman Jones. — W. C. Roberts Austen.
Henry C. Jenkins. — William A. Tilden.
T. E. Thorpe. — A. Liversidge.

Walford, Samuel Matthew,

62, Bloom Street, Stockport,

Teacher of Chemistry. Chemistry Master at the Oldham Municipal and the Borough of Hyde Technical Schools. Science Master, Standard Grammar School. Have been similarly engaged about eight years. Studied Chemistry at Owens College, Manchester, and have attended courses in Chemistry and Metallurgy at the Royal College of Science, London. "Roscoe Exhibitioner" and "Chemistry Prizeman" of the Union of Lancashire and Cheshire Institutes. First Honours, Chemistry, Science and Art Department.

H. B. Dixon. — Bevan Lean.
G. H. Bailey. — W. H. Perkin, jun.
A. Harden.

Walker, James Wallace, M.A., Ph.D.

Demonstrator in Chemistry, University College, London. Author and joint author with Professor Purdie of several papers which have appeared in the *Transactions* of the Chemical Society.

Thomas Purdie. — William Ramsay.
Morris W. Travers. — John Shields.
J. Norman Collie. — Sidney Williamson.

Wilderman, Meyer,

Davy-Faraday Laboratory, Albemarle Street, London.

Engaged in Scientific research in Physical Chemistry at present in the Davy-Faraday Laboratory at the Royal Institution. *Zeitschrift für Physikalische Chemie*, viii., ix., xi., xiv., xiv., xv., xv., xix., xix.; *Phil. Mag.*, July, 1895; *Transactions* of the Chemical Society, 1897, *Proceedings* of the Royal Society, 1896, *Berichte der Deutscher Chem. Ges.* 1890, 1891; *Journal für praktische Chemie*, &c.

A. Vernon Harcourt.	Wyndham R. Dunstan.
Herbert McLeod.	R. Meldola.
Robert Mond.	*T. E. Thorpe.*

The following Candidates are recommended by the Council under Bye-law I. (3).

Aquino, Thomas Hannibal,

Gadag, Dharwar District, India.

Assistant Surgeon, Bombay Medical Service. Licentiate of Medicine and Surgery, Bombay University. Late Teacher of Chemistry, Toxicology, and Materia Medica, Hydrabad Medical School, Sind. Member Indian Medical Association and British Medical Association. Winner of Sir Jamsetji Jijibhoy's "Medical Prize" in Medicine and Surgery, "Hunter Prize" in Ophthalmology, and "Cama Prize" for the best essay on the Sewerage of Bombay, awarded by the University of Bombay in 1884.

S. M. Kaka, D.P.H.

Bhaduri, Jyoti Bhushan,

Presidency College, Calcutta, India.

Lecturer, Presidency College. M.A. in Physics, Roy Prem Chand Scholar in Chemistry; Elliott Medallist for Original Investigation in Chemistry. Contributions: "On the Decomposition of Hydrochlorites." "Notes on the Estimation of Chlorine." Published in the *Journal* of Asiatic Society, Bengal 1896. "Note on the action of Nitric Acids on Alkali" in conjunction with Mr. Pedler, F.R.S., not yet published, but read on November 4th, 1896.

Alexander Pedler.

Rutter, Alfred,

Broken Hill, New South Wales, Australia.

Metallurgical Chemist. Chemist to the Broken Hill Proprietary Co. Associate of the Royal College of Science.

T. E. Thorpe. W. C. Roberts Austen.

Unwalla, Rustomji Navroji,
Bhavnagar, Kathiawar, India.

Assistant Doctor and Chemical Analyser, Bhavnagar State Medical Department. Student Grant Medical College for 10 years. Passed in 1885 First Examination in L.M. and S., including Chemistry, Theoretical and Practical, Bombay University. Passed Final L.M. and S. fully in Medical Jurisprudence and Toxicology. Special work under Chemical Analyser (Government), Bombay, and under Mr. Hankin, Government Bacteriologist and Chemical Analyser, Agra.

Arthur Richardson.

RICHARD CLAY AND SONS, LIMITED, LONDON AND BUNGAY.

Issued 2/3/1897.

PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

EDITED BY THE SECRETARIES.

No. 175. Session 1896–7.

February 18th, 1897. Mr. A. G. Vernon Harcourt, President, in the Chair.

Mr. E. Haynes Jeffers was formally admitted a Fellow of the Society.

Certificates were read for the first time in favour of Messrs. Herbert William Leyland Barlow, M.A., M.B., Holly Bank, Urmston, Manchester; Frederick Filmer de Morgan, Andely Lodge, Caeran Park, Newport, Monmouthshire; Louis Charles Deverell, Onslow House, Worthing; William James George Lasseter, B.A., 10, Stanley Road, Oxford; Harry Edward William Phillips, B.A., 47, Chalfont Road, Oxford; William Herbert Waite, B.A., Park Road, Halifax; Charles Thomas Foster Watts, 7, Cambrian Crescent, Chester; John Welsh, 12A, Seller Street, Chester.

The certificate of the following candidate, recommended by the Council under Bye-law I (3), was also read:—

Frederic Hewlett Burton-Brown, Simla, India.

It was announced that the following changes in the Officers and Council were proposed by the Council:—

As *President*—Professor James Dewar, M.A., LL.D., F.R.S., *vice* Mr. A. G. Vernon Harcourt, M.A., D.C.L., LL.D., F.R.S. As *Vice-Presidents*—Professor W. Ramsay, Ph.D., F.R.S., and Professor J. Emerson Reynolds, M.A., F.R.S., *vice* Professor James Dewar, M.A., LL.D., F.R.S., and Mr. Horace T. Brown, F.R.S. As *Ordinary Members of Council*—Messrs. C. T. Heycock, M.A., F.R.S.; Rudolph Messel, Ph.D.; Tom Kirke Rose, D.Sc.; and Alexander Scott, M.A., D.Sc., *vice* Messrs. Bernard Dyer, D.Sc.; G. Harris Morris, Ph.D.; W. A. Shenstone; and T. Stevenson, M.D.

It was also announced that the Council had awarded the Longstaff Medal to Professor William Ramsay, F.R.S., for the discovery of helium, and his share in the investigation of argon.

Messrs. H. Brereton Baker, F. D. Chattaway, and John Shields were appointed to audit the Society's accounts.

Of the following Papers, those marked * were read.

*18. "The formation of dithonic acid in the oxidation of sulphurous acid by potassium permanganate." By T. S. Dymond and F. Hughes.

When a solution of sulphurous acid is titrated with a solution of potassium permanganate, decolorisation of the permanganate ceases when only 89 per cent. of the quantity required to oxidise the sulphurous acid to sulphuric acid has been used. This is due to the formation of dithionic acid in addition to sulphuric acid. The proportion of dithionic acid produced is constant, and is not influenced by either the dilution or the temperature, or the acidity of the solution. Its production, therefore, appears to be an essential part of the reaction, and to be due to the weak oxidising action of the permanganate in a final stage of its reduction. The sulphuric and dithionic acids produced are in the proportion required by the supposition that manganese heptoxide is first reduced to the red oxide with production of sulphuric acid, and further reduced to the monoxide with production of dithionic acid. When, however, sulphurous acid is treated with the red oxide, sulphuric acid is the only product.

Discussion.

The President said that he had worked, a number of years ago, upon the reaction between solutions of potassium permanganate and sulphurous acid, before sodium thiosulphate had come into use for estimating iodine. In making determinations without excluding air from the water, he had found that the quantity of permanganate used was far less than the amount necessary for the complete oxidation of the sulphurous acid. He found that the sulphurous acid was oxidised by the atmospheric oxygen dissolved in the water, and so progressively as the water gradually dissolved the oxygen in the air lying over it. As the result of a number of experiments, he proved that the diminution in the quantity of permanganate required increased with the dilution of the sulphurous acid, and also that if the water was boiled until air-free the quantity of permanganate used was larger, but he had not obtained such constant results as Messrs. Dymond and Hughes. He had tried the experiment of adding a small quantity of manganous sulphate to the dilute solution, and had found that this salt also was

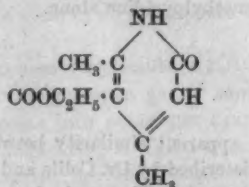
able to determine the oxidation of sulphurous acid by atmospheric oxygen. He thought the authors' experiments extremely interesting in showing the constant production of dithionic acid.

Dr. Scott thought it would be worth while to try the effect of manganic sulphate in oxidising sulphurous acid.

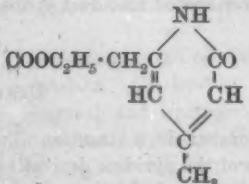
Professor Dunstan suggested that it would be interesting to determine whether the formation of dithionic acid occurred at the positive electrode during the electrolysis of a solution of sulphurous acid, since it seemed possible that the dithionic acid might be formed by the oxidation of sulphurous acid in much the same way as persulphuric acid was formed by the oxidation of sulphuric acid. He understood that in the remarkable action of manganous sulphate described by the President this salt undergoes no change.

***19. "On the production of pyridine derivatives from ethylic-β-amido-crotonate." By J. Norman Collie, Ph.D., F.R.S.**

Amongst compounds from which pyridine derivatives can be obtained, ethylic acetoacetate stands out prominently. The author has already called attention to the fact that, when ethylic β-amido-crotonate is distilled, various pyridine compounds are formed. When the hydrochloride of ethylic β-amido-crotonate is heated to a temperature of about 120°, it at once condenses according to the equation $2C_6H_{11}NO_2HCl = C_{10}H_{15}NO_3 + NH_4Cl + C_2H_5OH + HCl$. This compound, $C_{10}H_{13}NO_3$, is the ethylic ether of an oxylutidine: it melts at 138—139°. If in its production the hydrochloride of ethylic β-amido-crotonate be heated with one molecular quantity of ethylic β-amido-crotonate, $C_6H_{11}NO_2HCl + C_6H_{11}NO_2 = C_{10}H_{15}NO_3 + NH_4Cl + C_2H_5OH$, an isomeric ether is obtained, m. p. 166—167°. The acids obtained from these two ethers melt respectively at 300—304° and 190—191°, and both acids decompose at their melting point, lose carbon dioxide, and give pseudolutidostyril.



Ether, m. p. 139°.
Acid, m. p. 300°.
A.



Ether, m. p. 167°.
Acid, m. p. 190°.
B.

Ether A, when boiled with soda, only hydrolyses with considerable difficulty. It does not react with acetyl chloride, hydroxylamine,

or nitrous acids; strong sulphuric acid dissolves it on warming, but the substance is precipitated unchanged when the mixture is poured into water. With bromine, a mono-substituted derivative is produced, $C_{10}H_{12}NO_3Br$, m. p. 158—159°. With phosphorus pentachloride, a chloro-lutidine derivative results, $C_{10}H_{12}NO_2Cl$, which is an oil, b. p. 288—290°. After prolonged treatment with tin and hydrochloric acid, the chlorine is removed and replaced by hydrogen, and an α-γ-dimethyl-β-ethylic carboxylate of pyridine, b. p. 246—248°, is obtained.

The acid obtained by the hydrolysis of ether A is very insoluble in water, but can best be recrystallised from that solvent; various attempts were made to convert this acid into the isomeric acid obtained from ether B, but without result.

Ether B, which is isomeric with ether A, is hydrolysed at once when added to soda solution and warmed. It gives a compound with phenylhydrazine, and when boiled with strong hydrochloric acid is decomposed; it is much less stable than ether A.

With bromine, it gives a di-substituted product at once, $C_{10}H_{11}NO_3Br_2$. This compound, when treated with soda, gives the sodium salt of a dibromo-acid, which acid melts at 227—228° with complete decomposition. Ether B gives on hydrolysis an acid, m. p. 190—191°, which can easily be crystallised from hot water; when melted it decomposes quantitatively into carbon dioxide and pseudolutidostyril in exactly the same manner as the isomeric acid, m. p. 300—304°. Pseudolutidostyril, $C_5H_3(CH_3)_2NO$, which is a dimethylpyridine derivative, was first obtained by Hantzsch (*Ber.*, 1884, **17**, 2904) by the action of heat on a trimethylpyridine derivative. It was found on heating pseudolutidostyril with zinc dust, that although some dimethylpyridine (lutidine) was formed, the chief product of the reaction was a trimethylpyridine (collidine).

Pseudolutidostyril, when acted on by phosphorus pentachloride, gives α-γ dimethyl-δ-chloropyridine, b. p. 212—214°, and this compound when passed over heated zinc dust yields dimethylpyridine alone.

Discussion.

Dr. Forster drew attention to the apparent similarity between the reactions of the pyridine derivatives described by Dr. Collie and certain of the nitrogen derivatives of camphor when Tiemann's formula was employed.

Dr. Kipping was of opinion that there was no essential difference between Tiemann's formula for camphor and that proposed by Bredt. He thought that the possibility of the occurrence of tautomerism or

stereoisomerism in the compounds described by Dr. Collie should be kept in view.

Dr. Collie, in reply, said he had not gone completely into the details of the various reactions he had made use of in preparing these substances, and he thought that when the full paper was read it would be seen that the substances were actually different in constitution, and not merely tautomeric or stereoisomeric.

*20. "Sodamide and some of its substitution derivatives." By A. W. Titherley, M.Sc., Ph.D.

Sodamide in its reactions with organic haloid compounds invariably gives rise to complex decompositions without appreciable replacement of the halogen by NH_2. The hydrogen of the sodamide, and not the sodium, reacts, giving hydrochloric acid, which with the amide yields ammonia, whilst the group $NaN=$ remains more or less intact, being found afterwards as sodium cyanide and sodium cyanamide. Charring invariably occurs, even when the reaction is conducted with care.

Sodamide on treatment with organic substances possessing a weak acid tendency, such as oximes and hydrazines, readily reacts, giving ammonia and sodium derivatives. In benzene solution these are obtained usually as fine crystalline precipitates, which may sometimes be crystallised from boiling benzene. Sodium acetoxime, sodium hydrazobenzene, sodium phenylhydrazine, and others have been thus obtained.

A series of substitution derivatives of sodamide formed by the replacement of one or both hydrogen atoms in $NaNH_2$ have also been prepared by the interaction of sodamide with (1) Aromatic amines; (2) Amides, according to the general equations:—(*a*) $NaNH_2 + R{\cdot}NH_2 = NaNH{\cdot}R + NH_3$; (*b*) $NaNH_2 + R{\cdot}CONH_2 = NaNH{\cdot}CO{\cdot}R + NH_3$.

In the former case, the reaction is conducted with the substances in the free state in an atmosphere of coal gas, and in the latter, in benzene solution.

Potassium ethylamide, $KNHC_2H_5$, is formed by the careful action of ethylamine gas upon gently heated potassium. On heating, it readily decomposes into potassium cyanide, charcoal, and hydrogen. Sodium phenylamide, $NaNH{\cdot}C_6H_5$, sodium diphenylamide, $NaN(C_6H_5)_2$, sodium *p*-tolylamide, sodium *β*-naphthylamide, &c., are all very readily prepared by the above general reaction. They form white, greenish-yellow, or brown, amorphous solids with conchoidal fracture, or light yellowish powders, which are blackened and decomposed quickly in the air, darkening especially when moistened with benzene.

When sodamide reacts with organic amides (best in boiling benzene

solution) ammonia is rapidly evolved, and the substituted sodamides are obtained as fine, white, crystalline solids, those of larger molecular weight being appreciably soluble in benzene.

Sodium formamide, $NaNH \cdot CO \cdot H$, sodium acetamide, $NaNH \cdot COCH_3$, sodium propionamide, and sodium benzamide have been thus prepared —the latter apparently identical with the compound obtained by Curtius from the action of sodium upon benzamide by long-continued boiling in xylol solution.

The latter class of substituted sodamides are soluble without decomposition in alcohol, and their solutions, on treatment with alcoholic silver nitrate, throw down bright orange-red precipitates of the silver compounds, which are very unstable. From the colour of these silver derivatives, and the difficulty with which they and the sodium compounds appear to react with alkyl iodides, &c., the author concludes that the silver and sodium atoms, respectively, are directly attached to nitrogen, and that therefore the above derivatives are to be represented as possessing the ordinary amide and not the imido-hydroxy formula; the amides themselves are most probably tautomeric substances.

***21. "Rubidamide." By A. W. Titherley, M.Sc., Ph.D.**

Metallic rubidium behaves like the other alkali metals towards ammonia, displacing one atom of hydrogen and forming rubidamide $RbNH_2$. Though not so energetic as in the case of lithium, the action is very rapid and commences in the cold. On heating in a silver boat to between 200—300°, oily drops of the amide quickly form and flow to a liquid in which the metal floats and partly dissolves to a deep blue solution, at once decolorised and converted into rubidamide by the action of ammonia. Rubidamide crystallises in plates melting at 285—287°, higher than sodamide and potassamide, but lower than lithamide. At 400°, it distils undecomposed in a current of ammonia. With water, it is violently decomposed, giving ammonia and rubidium hydrate. Alcohol also decomposes it and its behaviour with organic substances is very similar to that of sodamide or potassamide.

***22. "On the spectrographic analysis of some commercial samples of metals, of chemical preparations, and of minerals from Stassfurt potash beds." By W. N. Hartley, F.R.S., and Hugh Ramage.**

In continuation of the work already published (*Roy. Soc. Proc.*, 1896, 60, 393, and *Proc.*, 1897, 13, 11), samples were examined of steel made at Middlesbrough from the blast furnace metal smelted from Cleveland clay ironstone, and rolled into rails; of alumina and 'red mud'

separated from bauxite at the British Aluminium Co.'s Works at Larne, and of the aluminium prepared from the alumina at Foyers and of various commercial alums.

It is shown that of the constituents of the blast furnace metal, the alkali metals, calcium, copper, silver, gallium, manganese, and lead are present also in the steel, but the chromium and nickel have been removed.

Of the constituents of bauxite, traces of sodium, potassium, calcium, copper, silver, gallium, iron, manganese, and lead are found in the metallic aluminium. These elements are also present in larger quantities in the 'red mud' and in addition nickel and chromium are present.

The Alums.—Examined directly, by heating 0·5 gram of the dried sample in the oxyhydrogen flame, sodium, potassium, rubidium, calcium, and thallium are found as common constituents, and copper, gallium, iron, and nickel as occasional constituents. More interesting results were obtained by examining the precipitates produced by potassium ferrocyanide in solutions, containing 50 grams of the alum, strongly acidified with hydrochloric acid. These precipitates contained the elements sodium, potassium, rubidium, cæsium, copper, silver, calcium, gallium, thallium, nickel, manganese, besides iron, which was also present in the acid radical. The rubidium, cæsium, gallium, and thallium lines are strong in some of the spectra, and the results indicate that these elements are almost wholly precipitated by this process. A sample of "aluminoferric" from Messrs. Spence and Sons, Manchester, contained all the elements found in the alums, but in much larger quantities. Of these elements, the pyrites furnishes the thallium and also a trace of indium found in a bye-product of the manufacture of alum, whilst the other elements were traced to the aluminous minerals, bauxite and shale. The shale was richer in alkalis and gallium than the bauxite, but a sample of French bauxite was richer in silver and lithium than either Irish bauxite or shale.

Samples of Stassfurt minerals were examined in the course of the investigation, and were found to yield spectra containing no lines of rubidium, cæsium, gallium, or thallium. These salts gave only weak lines of a few elements besides the lines of the principal elements composing them.

It is pointed out in the paper that the elements found by their spectra actually exist in the specimens, as there is no possibility of them being accidentally introduced, and furthermore, substances have been examined which have given no trace even of such widely distributed elements as potassium and calcium and in which the D lines are very weak.

The systematic examination of railway metal by such an analytical

method as is here employed might lead to results of practical importance. The method reveals the presence of small quantities of metals such as copper, silver, gallium and lead, which have not been considered in dealing with commercial irons, and the influences of which upon the physical properties of these have not been studied.

Discussion.

Dr. Rideal suggested that the calcium present in aluminium and its compounds might be derived from the vessels employed in the manufacture as well as from the bauxite. He thought it probable that calcium might be present as metal in commercial specimens of aluminium.

23. "Dissociation pressure of alkylammonium hydrosulphides." By James Walker, D.Sc., Ph.D., and John S. Lumsden, B.Sc., Ph.D.

The dissociation pressures of ammonium, ethylammonium, and dimethylammonium hydrosulphides have been determined, as well as the dissociation pressures of mixtures of these substances in pairs. The values obtained for the mixtures fell in every case considerably below the values calculated from the dissociation pressures of the components by the law of mass action. The ratios of the dissociation pressures of these substances, whether simple or mixed, are independent of the temperature, a fact which proves their heats of dissociation to be equal.

24. "Supposed condensation of benzil with ethyl alcohol. A correction." By Francis Robert Japp, F.R.S.

The author finds that the compound, described by him in a paper published jointly with Miss Owens (Trans., 1885, 47, 90), as formed by the condensation of benzil with ethyl alcohol, is in reality identical with Japp and Miller's *anhydracetonedibenzil*, $C_{31}H_{24}O_4$ (m. p. 194—195°), and that its formation was due to the presence of acetone in the "methylated spirit" (alcohol "denatured" with 10 per cent. of crude wood-spirit), which was used instead of duty-paid alcohol, in the preparation of the compound. The formula, $C_{30}H_{24}O_4$, ascribed to the condensation compound requires analytical figures differing only very slightly from those required by anhydracetonedibenzil.

At the time the paper was published, the authors believed the compound to be identical with Limpricht and Schwanert's *ethyldibenzoïn*, $C_{30}H_{26}O_4$, which Jena stated that he had prepared by the action of alcoholic potash on benzil—the reaction employed by the authors. On the strength of this belief, they proposed to alter Limpricht and Schwanert's

formula to $C_{20}H_{24}O_4$, and they further cast doubt on the existence of an acetyl derivative which these investigators had prepared.

The author regrets the publication of these perfectly baseless criticisms on Limpricht and Schwanert's work.

The author is indebted to Professor Alexander Smith for privately informing him that he had not succeeded in preparing the compound from benzil and alcohol, and thus calling his attention to the matter.

25. "The viscosity of mixtures of miscible liquids." By T. E. Thorpe, F.R.S., and J. W. Rodger.

The authors having measured the viscosity of a large number of liquids, mostly carbon compounds and of very different types, at various temperatures up to the boiling points under a standard atmosphere (*Phil. Trans.*, 1894, 185A, 379; 1897, 189A), have made observations on mixtures of chemically indifferent and miscible liquids, with the view of throwing light on the relation of the viscosity of a mixture to the viscosity of its constituents. A sufficiently comprehensive study of this question would afford answers to many questions of interest. Thus it would settle whether viscosity was related to the number of molecules per unit volume or per unit surface, and would indicate, therefore, how viscosity observations, and indeed all observations which depend upon surface effects, should be treated. It would also indicate whether, in the case of a mixture of a simple and a complex liquid, the values of the viscosity gave any indication of the decomposition of molecular aggregates, and how such decomposition was related to dilution and temperature.

On the present occasion, the authors communicate the results of a series of measurements made at different temperatures on mixtures of carbon tetrachloride and benzene, methyl iodide and carbon disulphide, and ether and chloroform, the last pair of which they studied on account of the relatively considerable evolution of heat which accompanies their admixture. The methods of observation and of reduction were the same as those previously employed, and the apparatus was identical with that already described (*loc. cit.*).

In no case could the density of the mixture be calculated by the ordinary admixture rule. Carbon tetrachloride and benzene contract on mixing, as already found by F. D. Brown (Trans., 1881, 39, 207); whereas methyl iodide and carbon disulphide expand. Ether and chloroform contract considerably.

As regards viscosity, the observations afford additional evidence of the fact indicated by Wijkander and supported by Linebarger, that the viscosity of a mixture of miscible and chemically indifferent liquids is rarely, if ever, under all conditions, a linear function of the com-

position. It seldom happens that a liquid in a mixture preserves the particular viscosity it possesses in the unmixed condition. To judge from the instances hitherto studied, the viscosity of the mixture is, as a rule, uniformly *lower* than the value calculated on the assumption that each constituent exercises an influence proportional to its amount, although many examples are known to the contrary. No simple relation can as yet be traced between the viscosity of a mixture and that of its constituents.

In the case of a mixture of ether and chloroform, the viscosity at low temperatures is *greater* than the admixture rule would indicate, but as the temperature is raised, or as the mixture giving the maximum contraction is diluted, the viscosity eventually becomes *less* than the calculated value, when the general course of the curve showing the relation of viscosity to composition resembles that of such mixtures as carbon tetrachloride and benzene, or of methyl iodide and carbon disulphide. The phenomena in the case of a mixture of ether and chloroform would seem, to begin with, to be analogous to those of a mixture of ethyl alcohol and water, but the condition which determines the contraction and the maximum viscosity, whether it be a feeble chemical combination or a molecular aggregation of a purely physical character, is destroyed by heat or dilution.

26. "Magnesium nitride as a reagent." By H. Lloyd Snape, D.Sc., Ph.D.

The object of the experiments detailed in this paper was to investigate whether magnesium nitride could be utilised to introduce nitrogen in the place of oxygen, chlorine, and other negative elements which combine with magnesium. The author investigated the behaviour of magnesium nitride towards chloroform, carbon trichloride, and benzaldehyde respectively, in the hope that the reactions represented by the following equations would occur:—(1) $2CHCl_3 + Mg_3N_2 = 3MgCl_2 + 2HCN$; (2) $C_2Cl_6 + Mg_3N_2 = 3MgCl_2 + C_2N_2$; (3) $3C_6H_5\cdot CO\cdot H + Mg_3N_2 = 3MgO + (C_6H_5\cdot CH)_3N_2$. The substances to be treated with magnesium nitride were sometimes passed in the form of vapour over the latter compound, and sometimes directly mixed with it, the mixture being heated in a sealed tube.

In no case was the desired nitrogenous compound obtained. The chloroform was not attacked at temperatures at which hydrocyanic acid could exist without decomposition, but at higher temperatures an energetic reaction took place, and the observed results were consonant with the reaction $2CHCl_3 + Mg_3N_2 = 3MgCl_2 + C_2 + N_2 + H_2$. Carbon trichloride and benzaldehyde were likewise unaffected at temperatures below those at which the anticipated products could be formed. On

heating with benzaldehyde to about 240°, a crystalline product, identical with that described by Laurent as amarone, was obtained. Both were subsequently discovered to be identical with the substance named tetraphenylazine by Japp and Burton. (See also the following paper.)

27. "The identity of Laurent's amarone with tetraphenylazine." By H. Lloyd Snape, D.Sc., Ph.D., and Arthur Brooke, Ph.D.

Amarone being required to compare with the substance obtained, as described in the preceding paper, by the action of magnesium nitride upon benzaldehyde, the authors repeated Laurent's experiments.

It was necessary, in the first instance, to prepare benzoylazotide. This, it was found, could be more readily prepared than by the methods previously given, by the action of ammonium cyanide upon benzaldehyde. Laurent had stated that benzhydramide was produced by the long continued action of ammonium cyanide upon benzaldehyde, but this was probably due to his having employed an excess of the former reagent. The formula given by Laurent to benzhydramide would accord with its formation by treating benzoylazotide with benzaldehyde, $C_6H_5 \cdot CO \cdot H + C_{15}H_{12}N_2 = C_{22}H_{18}N_2O$. The authors propose to try whether such a reaction can actually be carried out. The vapours of ammonium cyanide were conducted into a mixture of benzaldehyde and alcohol. Crude benzoylazotide slowly separated out, and was washed with alcohol and recrystallised from benzene. The crystals softened at 198°, and completely melted, with attendant decomposition, at 202°. They were readily soluble in benzene and chloroform; difficultly soluble in alcohol and carbon disulphide, scarcely at all soluble in ether, and insoluble in water. An estimation of nitrogen established their identity with the benzoylazotide previously obtained by other methods.

To prepare amarone, benzoylazotide was next subjected to dry distillation under a pressure of 21 mm. The residue left, after hydrocyanic acid and other comparatively volatile vapours had been removed, was crystallised from alcohol containing a small quanity of hydrochloric acid, and washed with some more of the same solution to extract any residual lophine. The crystals which were left melted at 243 to 244°, dissolved in concentrated sulphuric acid giving the characteristic red solution, and behaved towards other solvents precisely in the same manner as the crystalline substance previously prepared from magnesium nitride and benzaldehyde.

By analysis, it was found that the empirical formula of amarone was $C_{14}H_{10}N_2$, not $C_{16}H_{11}N$, as had been stated by Laurent. The amarone which he obtained was evidently not pure, its melting point being only 233°, or about 10° lower than that of the purified material.

Moreover, a comparison of the properties of pure amarone showed it to be identical with the substance named by Japp and Burton tetraphenylazine, $C_{28}H_{20}N_2$. The authors were kindly supplied by Professor Japp with some of the latter compound, prepared by him from benzoin, for the purpose of instituting this comparison. It was thus established that amarone, as described by Laurent, was actually tetraphenylazine.

It seems probable to the authors that the substance obtained by Curtius and Blumer having the same empirical formula, $C_{14}H_{10}N$, to which they have not assigned a structural formula, will likewise prove to be tetraphenylazine. The properties of this compound, so far as they have been described, agree with this supposition.

28. "Studies on the interaction of highly purified gases in presence of catalytic agents. Part I." By Wm. French, M.A.

In absence of light, spongy platinum does not appear to bring about combination between oxygen and hydrogen if they have been previously carefully dried; and, so far, experiments seem to show that, after the gases have been in contact with the platinum, added moisture does not cause an explosion.

29. "Contributions to the knowledge of the β-ketonic acids. Part III." By S. Ruhemann, Ph.D., M.A.

The author arrives at the conclusion, from the further study of the action of ethylic chlorofumarate and ethylic α-chlorocrotonate on ethereal salts of β-ketonic acids, that the substances described before (Trans., 1896, **69**, 530, 1383) are to be regarded as ketone-compounds, and he gives the corrections necessitated by the change of view concerning the constitution of the various products there recorded. He further shows that the substance formed from ethylic chlorofumarate and ethylic acetomethylacetate is to be looked upon as ethylic acetoallylenedicarboxylate, $CH_3\cdot CO\cdot C(COOC_2H_5):C:CH\cdot COOC_2H_5$. Aniline acts on this ethereal salt with formation of an anile-compound which crystallises in yellow plates (m. p. 180°).

Ethylic benzoylacetate and ethylicacetonedicarboxylate form, with ethylic α-chlorocrotonate, compounds which are to be represented by the formulæ

$C_6H_5\cdot C(OH):C\cdot COOC_2H_5$
$CH_2\cdot CH:C\cdot COOC_2H_5$

Ethylic benzoylbutylenedicarboxylate.

and

$COOC_2H_5\cdot CH_2\cdot CO\cdot CH\cdot COOC_2H_5$
$CH_2\cdot CH:C\cdot OOC_2H_5$

Ethylic malonylbutylenetricarboxylate.

The latter substance, under the influence of ammonia, yields two isomeric diamides of the ethereal salt, having the formula $C_{11}H_{16}N_2O_5$, besides a diamide of the corresponding acid.

30. "Contributions to the knowledge of the β-ketonic acids. Part IV." By S. Ruhemann, Ph.D., M.A., and A. S. Hemmy, B.A., M.Sc.

Ethylic acetosuccinate was found to give a colour reaction with ferric chloride, in opposition to the statement of Conrad (*Annalen*, 1877, **188**, 218). The authors give an account of various substances formed from this ethereal salt under the influence of ammonia and of phenylhydrazine. In the latter case, ethylic methylphenylpyrazolone acetate is formed, which, on hydrolysis, yields the corresponding acid. The bromo-derivative of ethylic acetosuccinate was prepared, and on distillation in a vacuum gave ethylic carbotetrinate (*cf.* Moscheles and Cornelius, *Ber.*, 1888, **21**, 2603).

Ethylic benzoylsuccinate, obtained according to Perkin's directions (Trans., 1885, **47**, 272), was found to distil without decomposition at 192—193° at 10 mm., and to be decomposed by ammonia with formation of succinamide.

31. "Oxidation of phenylstyrenyloxytriazole." By George Young, Ph.D.

The oxidation by alkaline potassium permanganate of phenylstyrenyloxytriazole, $C_6H_5{\cdot}CH{:}CH(C_6H_5){\cdot}C_2N_3{\cdot}OH$, yields phenyloxytriazole carboxylic acid, $C_6H_5{\cdot}C_2N_3(OH)CO_2H$. This acid, immediately on liberation, loses carbon dioxide and forms phenyloxytriazole, $\begin{matrix} C_6H_5{\cdot}N{\cdot}N \\ | \\ HC{:}N \end{matrix}\!\!>\!\!COH$.

The following derivatives of the carboxylic acid have been prepared. Ethylic phenylethoxytriazole carboxylate, $Ph{\cdot}C_2N_3(OEt)CO_2Et$, white needles, m. p. 82—83°. Amide, $C_6H_5{\cdot}C_2N_3(OC_2H_5)CONH_2$, white needles, m. p. 149—150°. Silver salt, $C_6H_5{\cdot}C_2N_3(OC_2H_5)CO_2Ag + 2H_2O$. Phenylethoxytriazole carboxylic acid, when liberated, loses carbon dioxide and forms phenylethoxytriazole, $C_6H_5{\cdot}C_2N_3H{\cdot}OC_2H_5$, needles, m. p. 60°. This compound has also been formed by the action of ethyl iodide on the silver derivative of phenyloxytriazole.

32. "Apiin and apigenin." (Preliminary notice). By A. G. Perkin.

Apiin, a constituent of parsley (*Apium petroselinum*), was first isolated by Braconnot (*Ann.*, 1843, **48**, 349), and subsequently examined by Planta and Wallace (*Ann.*, 1850, **74**, 262), who found it consisted of a glucoside. Gerichten (*Ber.*, 1876, **9**, 1124), in a more detailed investi-

gation, assigned it the formula $C_{27}H_{32}O_{16}$, and considered its decomposition by dilute acids to be most probably represented by the equation $C_{27}H_{32}O_{16} + H_2O = C_{15}H_{10}O_5 + 2C_6H_{12}O_6$, which is based upon the yield of apigenin thus obtained. He described no derivatives of apigenin, but states that by the action of alkali there is produced phloroglucol and an acid, which by prolonged treatment, is decomposed with formation of protocatechuic acid, *p*-hydroxybenzoic acid, formic and oxalic acids.

Having suspected, from a description of its properties, that apigenin was a yellow colouring matter, and this having been proved to be the case, the present investigation was instituted. It is wished to reserve the further study of the reactions of this interesting substance.

The glucoside apiin is somewhat difficult to fully decompose by dilute acids, the apigenin produced after 3 hours' digestion with hydrochloric acid of sp. gr. 1·04 yielding C = 64·3; H = 3·90; after 10 hours, C = 65·81, 65·74; H = 3·45, 4·01; and only when so treated for 25 hours are numbers obtained indicating the formula $C_{15}H_{10}O_5$, evidently the correct one. Calc., C = 66·66; H = 3·70; Found, C = 66·34, 66·37; H = 3·87, 3·81. Apigenin contains no methoxy-groups, and does not combine with mineral acids; it, however, forms a sulphonic acid not yet thoroughly examined. Dibromapigenin crystallises in almost colourless needles, melting above 290°. $C_{15}H_8O_5Br_2$ requires C = 42·05; H = 1·87; Found, C = 42·09; H = 2·23; and a tribenzoyl compound, $C_{15}H_7O_5(C_7H_5O)_3$, needles, m. p. 210—212° has also been obtained. Calc., C = 74 23; H = 3·78. Found, C = 74·41; H = 4·17. Apigenin reacts with diazobenzene, forming $C_{15}H_8O_5(C_6H_5N_2)_2$, orange-red needles, m. p. 290—292°. Calc., C = 67·78; H = 3·74; N = 11·71. Found, C = 67·22; H = 3·75; N = 11·54, 11·56; which yields a monacetyl derivative $C_{15}H_7O_5(C_2H_3O)(C_6H_5N_2)_2$; orange-red leaflets, m. p. 259—260°. Calc., C = 66·92; H = 3·84. Found, C = 66·66; H = 4·05. Experiments on the further acetylisation of this substance are in progress. By treatment with strong alkali, there is obtained from apigenin, phloroglucol, an acid, m. p. 208—209°, probably *p*-hydroxybenzoic acid, a trace of acetic acid, and a substance crystallising in colourless needles, m. p. 107°, which bears some resemblance to *p*-hydroxyacetophenone. Fuming nitric acid decomposes apigenin, the principal product being an acid; yellow needles, m. p. 244—245°. The dyeing properties of apigenin will be described in the full communication. The investigation of these substances will be continued, and the study of the ethylation and methylation of apigenin is also in progress.

33. "Note on the constitution of the so-called 'nitrogen iodide.'" By J. W. Mallet, F.R.S.

Mr. Chattaway concludes his paper by saying that "at present the formula NH_3I_2 seems best to accord with the reactions of the compound as a whole, and best to group all the known facts regarding it." Reference to a short paper by my sometime student, Mr. W. H. Seamon, published in the *Chemical News*, 1881, 44, 188, will show that a very different substance—liquid, and non-explosive—gives results on analysis agreeing well with this formula. It was obtained by the action of dry, gaseous ammonia on solid iodine, and appears to be identical with the substance prepared in a different way by Guthrie, of which brief mention is made by Mr. Chattaway in a footnote.

I cannot agree with him that in the explosive compound the ratio of N:I is always 1:2. Some analytical results of my own (published in the paper on this subject in the *American Chemical Journal*, 1879, 1, 4) were quite incompatible with this ratio, and agreed nearly with the ratio 1:3. In view of the fact that the preparation which gave these results had been freely washed with alcohol and afterwards with ether, I cannot think it probable that any considerable formation and retention of iodoform raised the proportion of iodine.

In any discussion of the composition of the explosive substance in question, some attention ought surely to be given to the probable analogy with nitrogen trichloride, for which Gattermann seems to have fairly well established the formula.

CERTIFICATE OF CANDIDATE FOR ELECTION AT THE NEXT BALLOT.

The Certificate of the following Candidate is recommended by the Council under Bye-law I. (3).

Burton-Brown, Frederic Hewlett,

C/o Surgeon-General, Government of India, Simla.

Surgeon-Captain, Indian Medical Service. M.A. Oxford. At present engaged in the study of the Indian Materia Medica. Late Demy (Natural Science), Magdalen College, Oxford; 1st Class, Honour School Natural Science, Oxford, 1886. Late Professor of Materia Medica, University of the Punjab. Author of "A Note on the Chemistry of Milk with reference to Hammersten's Investigations on

Casein," published in the *Proceedings of Physiological Society*, 1886. Worked in 1883–4 in Laboratory of the late Professor C. Fr. W. Krukenberg, of Jena. The results of investigations undertaken for the professor were published in his *Die vergleichende Physiologie*; these referred to the spectra of certain organic compounds.

Wyndham R. Dunstan.

At the next Meeting, on Thursday, March 4th, there will be a ballot for the election of Fellows, and the following Papers will be received. The authors of those marked with an asterisk have announced their intention of being present.

* "Some hydrocarbons from American petroleum. I. Normal and Iso-pentane." By Sydney Young, D.Sc., F.R.S., and G. L. Thomas, B.Sc.

* "The vapour pressures, specific volumes and critical constants of normal pentane; with a note on the critical point." By Sydney Young, D.Sc., F.R.S.

* "On the freezing-point curves of alloys containing zinc." By C. T. Heycock, F.R.S., and F. H. Neville.

* "The oxides of cobalt and the cobaltites." By A. H. McConnell and E. S. Hanes.

PASTEUR MEMORIAL LECTURE.

The Pasteur Memorial Lecture will be delivered by Professor Percy Frankland, Ph.D., F.R.S., at an extra meeting of the Society on Thursday, March 25th, at 8 p.m.

ANNIVERSARY MEETING.

The Anniversary Meeting will be held on Wednesday, March 31st, at 3 o'clock in the afternoon.

ANNIVERSARY DINNER.

It has been arranged that the Fellows of the Society and their friends shall dine together at the Criterion Restaurant on Wednesday, March 31st, at 7 p.m. *The Secretaries will be glad to receive early notification from those Fellows who intend to be present.*

RICHARD CLAY AND SONS, LIMITED, LONDON AND BUNGAY.

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No. 176. Session 1896–7.

March 4th, 1897. Mr. A. G. Vernon Harcourt, President, in the Chair.

Certificates were read for the first time in favour of Messrs. Alaric Vincent Colpoys Fenby, B.Sc., Hutton Grammar School, Preston; R. Glode Guyer, 20 Queen's Road, St. John's Wood, N.W.; Tom Mitchell, Cemetery House, Shaw, near Oldham; Robert Howson Pickard, B.Sc., Southfield, Priory Road, Edgbaston, Birmingham.

Mr. Cassal asked whether the officers had withdrawn the Certificate of a Candidate from the list to be balloted for that evening.

Professor Thomson stated that the Certificate of one of the Candidates had been postponed pending further information.

Dr. Armstrong remarked that such action had been taken by the officers on former occasions, and was within their discretion.

The following were duly elected Fellows of the Society:—Messrs. John Owen Alexander; Thomas Hannibal Aquino; William Arbuckle; John B. Ashworth; John Barclay, B.Sc.; Frank Bastow; Jyoti Bhushan Bhaduri, M.A.; James Herbert Brown; F. Hewlett Burton-Brown, M.A.; Alfred Cartmell; Masumi Chikashigé, B.Sc.; Alfred Foster Cholerton; Clarence Hamilton Creasey; James Crowther, B.Sc.; William Alfred Davis; William Diamond; John Wallis Dodgson, B.Sc.; Lawrence Dufty; William Buckland Edwards; Joseph Lake Gibbons; Alexander W. Gilbody, M.Sc., Ph.D.; Harold Walter Gough, B.A.; Ernest Goulding; Edward Graham Guest, M.A.; Vaughan Harley, M.D.; Ernald G. Justinian Hartley, B.A.; Thos. Hartley; Charles Heppenstall; John Holmes; Fred Ibbotson, B.Sc.; William Rose Innes, B.Sc., Ph.D.; David Smiles Jerdan, M.A., B.Sc.; Harold Johnson; Otis C. Johnson; Herbert King; William Robert

Lang, B.Sc.; Theophilus Henry Lee; Charles Henry Martin; Barker North; Charles Henry Parker; Samuel Pollitt, B.Sc.; Herbert Spindler Pullar; William Ralston, B.Sc.; John Stewart Remington; Edward Rosling; Alfred Rutter; Frank Southerden; William James Stainer, B.A.; Henry Potter Stevens, B.A.; Leonard Sumner, B.Sc.; Harry Thompson; Andrew Turnbull, Ph.D.; Basil William Turner; Rustomji Navroji Unwalla; Samuel Matthew Walford; J. Wallace Walker, M.A., Ph.D.; and Meyer Wilderman, Ph.D.

In accordance with the bye-law, the lists of the names of the Fellows recommended for election as official and ordinary Members of Council were read from the Chair.

Of the following Papers, those marked * were read.

***34. "Some hydrocarbons from American petroleum. I. Normal and Iso-pentane." By Sydney Young, D.Sc., F.R.S., and G. L. Thomas, B.Sc.**

The two pentanes were separated by fractional distillation from the "pentane" supplied by Merck of Darmstadt. This substance, which is obtained by the distillation of American petroleum, is a complex mixture of butanes, pentanes, and hexanes, with some benzene and a little hexanaphthene. A combination of a dephlegmator with a constant (or rather 'regulated') temperature still-head was employed; the apparatus is fully described in the paper.

Some of the constants of isopentane were determined so as to compare them with those of the two specimens prepared synthetically: the agreement was found to be very satisfactory. The boiling points under normal pressure are:—isopentane 27·95°; normal pentane 36·3.° The specific gravities at 0° are:—isopentane 0·63930, normal pentane 0·64539.

***35. "The vapour pressures, specific volumes and critical constants of normal pentane; with a note on the critical point." By Sydney Young, D.Sc., F.R.S.**

The critical temperature of normal pentane is 197·2°, the critical pressure is 25,100 mm. and the critical volume of a gram 4·303 c.c. The vapour pressures and specific volumes were determined from low temperatures to the critical point, and the observations were taken as near to the critical point as possible (197·15°), in order to obtain more complete experimental evidence regarding the condition of a substance at and very near that point.

The ratios of the absolute temperatures (boiling points) and volumes

to the critical constants, also the ratio of the actual to the theoretical density at the critical point (3·765), lead to the conclusion that, at the critical temperature and in the liquid state, the molecules are simple, like those of the gas.

Discussion.

The President said that for many years he had been interested in the isopentane derived from American petroleum, having proposed that its flame should be used, under specified conditions, as a standard of light. He had purified it by shaking with sulphuric acid, and afterwards with soda. He had no doubt it was an improvement to use nitric acid, as Dr. Young had done. He had used a dephlegmator very similar to that described, but had never succeeded by fractional distillation in obtaining a substance of such a constant boiling point as that obtained by Dr. Young. He was much interested to hear this proof by Dr. Young of the identity of isopentane with that which is obtained from amyl iodide, as experiments on the illuminating power did not quite settle this question.

Dr. Armstrong thought that it was not quite certain that the isopentane used by Dr. Young was a single thing, and it was probably very difficult to obtain satisfactory proof of purity. In the case of the specimen derived from amyl alcohol, he considered it likely that this was a mixture of two hydrocarbons, as it did not appear that the amyl alcohol of fusel oil had first been separated into its two constituents.

Dr. Craw said that Dr. Young seemed to have shown that the critical temperature could be determined accurately for the class of compounds on which he had worked; but he asked whether the critical temperature is capable of being determined with the same accuracy for all classes of compounds.

Mr. Groves agreed with Dr. Armstrong as to the necessity of taking special precautions in purifying materials and of not trusting to those supplied by manufacturers.

Dr. Thorpe said he had had some experience in the preparation of isopentane. He had obtained it from amyl alcohols of very different origin. The question was whether the isopentane derived from fusel oils of very different origin would give the same hydrocarbon. He had found that all the specimens of isopentane gave practically the same boiling-point and density numbers as those obtained by Dr. Young. Nevertheless, Mr. Rodger and he had found that the viscosities of isopentane derived from different sources varied considerably, and it was significant that their specific volumes and specific gravities agreed closely with those recorded by Dr. Young. In the case of other liquids differently prepared and purified, the same viscosity numbers

were obtained; for example, Professor Dunstan had provided him with a sample of pure ether and Dr. Perkin also provided him with a sample, and the viscosities of the two were in perfect agreement. Similarly, he had compared two samples of benzene of different origin, and here also the two samples gave the same viscosity number. On this account he was inclined to question the homogeneity of isopentane prepared from amyl alcohol.

Dr. Young, in reply, said he had spent many months in purifying the materials and was satisfied that they were pure. He was, indeed, surprised that doubt should be cast upon the matter.

In the fractionation of the pentane and isopentane, he started with considerable quantities of materials, about 1,500 grams, and he obtained about 110 grams of pure substance. The liquid was fractionated about 20 times, and the loss was nearly 20 grams in each fractionation. There were only, as far as he knew, three isomeric pentanes, and as they had distinctly different boiling points, he did not see that there could be any mistake as to their identity. The critical temperatures and pressures are very delicate tests of the purity of the substance. With slightly impure ether, the difference in critical pressure is very considerable.

With regard to the fractionation of pentane and isopentane, the ordinary methods of fractional distillation would not answer. With the ordinary still-head, the loss by evaporation was greater than the gain by distillation, but the regulated still-head he had used gave most satisfactory results. He had no hesitation in saying that, with all substances which do not undergo decomposition when heated, the critical point can be determined within one-tenth of a degree.

***36. "On the freezing-point curves of alloys containing zinc." By C. T. Heycock, F.R.S., and F. H. Neville.**

The paper is divided into two sections, the first dealing with cases where the freezing point of zinc is depressed by the addition of another metal, the second with the cases where it is raised by such an addition.

In section I, complete binary alloys of the following pairs of metals, zinc-cadmium, zinc-aluminium, zinc-tin and zinc-bismuth, are given. In the first three cases the metals appear to be miscible with each other in all proportions, but for zinc-bismuth the freezing-point curve shows the horizontal line of identical freezing points characteristic of the state when the alloy has separated into two conjugate liquids.

Taking the freezing point of zinc as 419°, the authors find for the temperatures of freezing and the composition of the eutectic mixtures the following

Alloy.	F.P.	Atomic percentage of Zinc.
Zn—Cd.	264·5	74
Zn—Al.	281	11
Zn—Sn.	198	84
Zn—Bi.	254·5	91·8

They do not consider that there is any indication of these metals combining chemically to form definite compounds when they are melted together.

Dilute solutions of the following metals in zinc were also examined: lead, thallium, antimony, magnesium.

The authors find that, with the exception of aluminium and cadmium, all the above-mentioned metals, when added in small quantities to molten zinc, cause the same atomic fall: that is, an alloy containing 1 atomic weight in solution in 99 atomic weights of zinc has a freezing point lower by 5·1° than that of pure zinc. Cadmium causes a somewhat smaller and aluminium a decidedly smaller depression. The atomic depression of 5·1°, when used with Van 't Hoff's equation for the latent heat, gives 28·3 calories for the latent heat of fusion of zinc, instead of Person's value of 28·13.

In section II, dilute solutions of copper and of gold in zinc are considered, and also a complete freezing point curve for all alloys of zinc and silver.

When small quantities of any one of these three metals are added to molten zinc the effect is the same: the freezing point is raised, and the whole mass of metal appears to solidify at a temperature above the freezing point of pure zinc. The rise in the freezing point, moreover, is proportional to the amount of the second metal present. But when as much as 2 atomic per cents. of silver or of copper or 3·3 of gold have been added the phenomenon alters, apparently abruptly. There are now two freezing points, a higher one which is very fugitive, and which is followed by the precipitation of much solid, and a lower one which is very constant, and which is independent of the amount of the added metal so long as the above-mentioned minimum is present. In the zinc-silver curve singularities are also found near 70 and 60 atomic per cents. of zinc, indicating the existence of more or less stable compounds, but the formula of these compounds is uncertain. Near 37·5 atomic per cents. of zinc there is another well-marked angle and a series of eutectic second freezing points, the phenomenon being possibly due to the separations of the alloy into conjugate liquids.

The authors also describe briefly some of the physical properties of the zinc-silver alloys, which appear to change in character at the angles of the curve.

The composition of the silver zinc alloys at each freezing point was

determined by extracting a portion in the liquid state, and estimating the percentage of silver by a volumetric analysis.

Discussion.

Mr. Newlands asked whether the formulæ of the compounds which were supposed to exist at certain points, viz., $AgZn$, $AgZn_2$, and $AgZn_3$, represented atoms of the metals, or only that the metals were present in that proportion.

Mr. Groves asked whether there was any connection between the colour of the silver-zinc alloy and any of the points on the curve.

Mr. Jenkins asked whether the colour of the alloy was in any way due to the effect of mechanical stress during sudden cooling.

Dr. Craw asked whether the atoms in the alloy were in the monatomic state, and whether the alloy might be compared with a solution.

Mr. Neville, in reply, said the formulæ were only empirical. They were disposed to think that the dissolved metal was in a monatomic state. The colour of the alloy did not seem to have any connection with the points on the curve, and although great mechanical stress occurred in its production, this did not seem to afford an explanation of the colour.

***37. "The oxides of cobalt and the cobaltites." By Arthur H. McConnell and Edgar S. Hanes.**

The authors describe a method for the preparation of alkali cobaltites, and show that cobalt forms an oxide, CoO_2, and an acid, H_2CoO_3, which have hitherto been looked upon as hypothetical, and a series of alkali salts on the type of potassium cobaltite, K_2OCoO_2. The conclusions the authors arrive at are as follows.

(1) That Durrant (Proc., 1896, **12**, 96, 244) has not produced sufficient evidence for the existence of either cobaltic acid or cobalt percarbonate.

(2) That cobaltous acid corresponds with cobalt dioxide, and forms alkali salts fairly stable in solution, which solutions have an unmistakable green colour.

(3) That cobalt forms a series of compounds with other metals in which the cobalt is part of the acid radicle.

(4) That cobaltous acid and cobaltites are strictly analogous to manganous acid and manganites, thus showing that the properties of cobalt are closely allied to those of the other elements associated with it in the periodic classification. Manganese is readily oxidised to the peroxide MnO_2, but cobalt much less readily yields the corresponding peroxide CoO_2.

(5) In view of the fact that cobalt dioxide does undoubtedly exist in a number of compounds, the authors suggest that the oxides of cobalt should be renamed, to bring them into line with the corresponding oxides of manganese.

(6) It is highly improbable that the formation of this green solution will prove to be of any use for the separation of cobalt from nickel, either quantitatively or qualitatively.

***38. "A new synthesis in the sugar group." By Henry J. Horstman Fenton, M.A.**

In previous communications, it has been shown that the acid (dihydroxymaleic acid) obtained by oxidation of tartaric acid in presence of iron decomposes, on heating with water, almost quantitatively into glycollic aldehyde and carbon dioxide. Also, that this aldehyde, when heated in a vacuum, undergoes condensation, yielding a sweet-tasting, solid gum which has the formula $C_6H_{12}O_6$.

The present paper describes an investigation which has been made upon the properties of this condensation product.

It is easily soluble in water, and its solution quickly reduces Fehling's solution and ammoniacal silver nitrate. It gives various colour-reactions characteristic of 'sugars,' and, after purification with alcohol, yields, with phenylhydrazine, a normal hexosazone, $C_{18}H_{22}N_4O_4$ melting at 168—170°. Heated with water to 140°, it yields furfural. It is optically inactive, and appears to be incapable of fermentation by yeast.

The purified 'sugar,' when further heated in a vacuum to 100—106°, loses water and becomes hard and brittle. After 2—4 hours' heating it has the composition $C_{12}H_{22}O_{11}$ and after 24 hours' heating the composition nearly approximates to $C_6H_{10}O_5$.

The conditions under which tartaric acid may be converted into dihydroxymaleic acid by atmospheric oxygen exhibit close analogies with some of the essential conditions of vegetable growth; and it is suggested that the direct production of a 'sugar' in the manner above indicated may possibly help to throw light upon the natural formation of carbohydrates.

39. "The dinitrosamines of ethylene aniline, the ethylene toluidines and their derivatives." By Francis E. Francis, Ph.D., B.Sc.

The dinitrosamine of ethylene aniline gives *p*-di-nitrosoethylene aniline hydrochloride on treatment with a mixture of glacial acetic and hydrochloric acids, and the resulting tetramine yields quinone on oxidation, showing that it is a *p*-diamine, ethylene *p*-phenylene diamine. The

di-nitrosamines of ethylene *o*-toluidine and ethylene *m*-toluidine yield di-nitroso compounds, which on reduction pass into corresponding tetramines, whereas the di-nitrosamine of ethylene *p*-toluidine is decomposed. This clearly shows that in the substances investigated the nitroso-group can only pass under the treatment described to the *p*-position in the benzene nucleus.

40. "Contribution to the knowledge of the β-ketonic acids." Part V. By S. Ruhemann, M.A., Ph D., and A. S. Hemmy, B.A., M.Sc.

Whilst studying the interaction between the sodium derivative of ethylic oxalacetate and ethylic chlorofumarate, the authors observed the formation of two isomerides of the formula $C_{14}H_{16}O_8$. One of them, melting with decomposition at 200°, forms blue salts with alkalis which, by an excess of the reagent, become colourless. The other, which melts at 123°, does not yield coloured salts, but gives a dark red coloration with ferric chloride. The authors arrive at the view that in the formation of these compounds, ethylic oxalacetate alone takes part, and they represent the constitution of the substance decomposing at 200° by the formula, $\begin{matrix} COOC_2H_5\cdot C \\ \| \\ OC\cdot COH \end{matrix} \begin{matrix} \equiv C\cdot COOC_2H_5 \\ | \\ C\cdot COOC_2H_5 \end{matrix}$ (ethylic anhydro-oxalaconitate), the other by the symbol, $\begin{matrix} COOEt\cdot C\cdot O\cdot COOEt \\ \| \quad\quad\quad\quad \| \\ HC\cdot CO\cdot C\cdot COOEt \end{matrix}$ (ethylic pyronetricarboxylate).

41. "Enantiomorphic forms of ethylpropylpiperidonium iodide." By Clare de Brereton Evans.

It has been found that ethylpropylpiperidonium iodide ($C_5H_{10}EtPrNI$) may be obtained from its solution in absolute alcohol, in right-handed and left-handed crystals. The enantiomorphism, however, is of a purely crystallogenic order, due to the arrangement of the molecules in the crystal, and not to the position of the atoms in space. This is proved by the optical inactivity of the substance in solution, as well as by the fact that either variety may be converted into the other by recrystallisation, the behaviour being like that observed in the case of sodium chlorate and bromate, &c., &c.

42. "Further note on ketopinic acid—pinophanic acid." By W. S. Gilles and F. F. Renwick.

The further investigation of the acid obtained by oxidising the solid hydrochloride from pinene with the strongest nitric acid (*Trans.*, 1896, 69, 1397), has brought to light a variety of interesting points.

Although bromine alone does not attack it, ketopinic acid is readily

brominated if a small quantity of phosphorus be present; the product has the formula $C_{10}H_{18}O_3Br$. (C = 46·18; 46·06; H = 4·96, 5·00; Br = 30·70. Calc. C = 45·98; H = 4·98; Br = 30·66). Monobromoketopinic acid melts at 181°; it is readily soluble in ether, acetone, acetic acid, and ethylic acetate, but sparingly so in benzene, chloroform, and hot water. When heated with aniline or quinoline, it is reconverted into ketopinic acid.

The hydroxime of ketopinic acid is merely hydrolysed when boiled with 50 per cent. sulphuric acid, being reconverted into ketopinic acid.

When cautiously fused with caustic soda, or even when boiled with an alcoholic solution of sodium ethylate, ketopinic acid is converted into a dibasic acid, *Pinophanic acid* of the formula $C_{10}H_{16}O_4$ (C = 60·14, 60·13; H = 7·86, 8·02; Ag in silver salt = 51·87, 52·03; Calc. C = 60·00; H = 8·00; Ag = 52·17). Pinophanic acid melts at 203°; it is insoluble in benzene, light petroleum, and chloroform, moderately soluble in hot water and hot ethylic acetate, and readily soluble in alcohol, acetone, and ether. Like ketopinic acid, it does not combine with bromine.

Although but slowly attacked, ketopinic acid is oxidised by prolonged digestion with neutral potassium permanganate solution. The product appears to be identical in composition with Kipping's camphotricarboxylic acid and Marsh and Gardner's camphoic acid, but more closely resembles the latter.

These acids are now being fully investigated.

43. "A synthesis of citric acid." By W. T. Laurence, B.A., Ph.D.

Ethylic citrate was obtained synthetically by the condensation of ethylic bromacetate with ethylic oxalylacetate in the presence of zinc, as indicated by the following equations:—(1) $COOEt\cdot CH_2Br + COOEt\cdot CH_2\cdot CO\cdot COOEt + Zn = COOEt\cdot CH_2\cdot C(OZnBr)(CH_2\cdot COOEt)\cdot COOEt$; (2) $COOEt\cdot CH_2\cdot C(OZnBr)(CH_2\cdot COOEt)\cdot COOEt + H_2O = COOEt\cdot CH_2\cdot C(OH)(CH_2\cdot COOEt)\cdot COOEt + ZnO + HBr$. The yield of ethylic citrate is very poor, owing to other reactions proceeding simultaneously. To further confirm the formation of ethylic citrate, it was converted into the calcium salt of citric acid, and a substance obtained showing the characteristic properties of calcium citrate. The same salt was also obtained by heating the zinc compound formed in equation No. 1 with alcoholic potash and precipitating the calcium citrate from the hot solution.

The results were all confirmed by analysis. The above synthesis of citric acid seems to be of interest as being more direct and simple than the synthesis from sym. dichloracetone or from ethyl γ-cyanacetoacetate.

ADDITIONS TO THE LIBRARY.

I. *Purchase.*

Hintze, Carl. Handbuch der Mineralogie. Zweiter band, Silicate und Titanate. Pp. x + 1841, mit 632 abbildungen im text. Leipzig 1897.

Brauns, Reinhard. Chemische Mineralogie Pp. xiii + 460, mit 32 abbildungen im text. Leipzig 1896.

Duclaux, E. Pasteur: Histoire d'un esprit. Pp. vii + 400. Sceaux 1896.

Engel, R., et Moitessier, J. Traité Élémentaire de Chimie Biologique, Pathologique, et Clinique. Pp. vii + 615, avec 102 figures intercalées dans le texte et 2 planches coloriées. Paris 1897.

Possetto, G. La Chimica del vino. Analisi, alterazioni, mani polazioni, adulterazioni. Pp. xvi + 496. Torino 1896.

Register of the Associates and old Students of the Royal College of Chemistry, the Royal School of Mines and the Royal College of Science, with Historical Introduction and Biographical notices, and portraits of Past and Present Professors by T. G. Chambers. Pp. cxxii + 231. London 1896.

II. *Donations.*

Arth. G. Recueil de Procédés de Dosage pour l'analyse des combustibles des minerais de fer, des fontes, des aciers, et des fers. Pp. iii + 313. Paris 1897. Two copies. From the Publishers.

Fresenius' Quantitative Analysis. Vol II., part IV. Translated by C. E. Groves, F.R.S. London 1897. From the Publishers.

PASTEUR MEMORIAL LECTURE.

The Pasteur Memorial Lecture will be delivered by Professor Percy Frankland, Ph.D., F.R.S., at an extra meeting of the Society on Thursday, March 25th, at 8 p.m.

ANNIVERSARY MEETING.

The Anniversary Meeting will be held on Wednesday, March 31st, at 3 o'clock in the afternoon.

ANNIVERSARY DINNER.

It has been arranged that the Fellows of the Society and their friends shall dine together at the Criterion Restaurant on Wednesday, March 31st, at 7 p.m. The President, Mr. A. G. Vernon Harcourt, in the Chair. *The Secretaries will be glad to receive early notification from those Fellows who intend to be present.*

At the next Meeting, on Thursday, March 18th, the following Papers will be received. The authors of those marked with an asterisk have announced their intention of being present.

* "On the atomic weight of carbon." By Alexander Scott, M.A., D.Sc.

* "On a new series of mixed sulphates of the vitriol group." By Alexander Scott, M.A., D.Sc.

* "The action of alkyl haloids on aldoximes and ketoximes." By Wyndham R. Dunstan, F.R.S., and Ernest Goulding.

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Issued 22/3/1897.

PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

EDITED BY THE SECRETARIES.

No. 177. Session 1896–7.

March 18th, 1897. Mr. A. G. Vernon Harcourt, President, in the Chair.

Messrs. H. P. Stevens, J. W. Walker, W. Arbuckle, N. T. M. Wilsmore, M. Wilderman, W. J. Pope, A. W. Crossley, H. R. Le Sueur, J. H. Miller, R. D. Littlefield, F. H. Neville, W. M. Heller, G. McGowan, C. M. Crossman, J. Holmes, and F. Southerden were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Alfred Hunter Boylau, Ellerslie, Richmond Road, Ealing, W.; Henry Norris Davidge, 37, Duke Street, Grosvenor Square, W.; Charles Henry Field, The Elms, Green Street Green, Orpington; Thomas Girtin, B.A., 125A, Highbury New Park, N.; James Jones, 117, Old Christchurch Road, Bournemouth; Charles MacCulloch, 395, Collins Street, Melbourne; George Fowlie Merson, 65, Northumberland Street, Newcastle; Thomas Tickle, 4, Packenham Street, W.C.

In accordance with the bye-laws, the following communication was read from the Chair:—

WE, the undersigned, beg to propose Prof. William Ramsay, Ph.D., F.R.S., as President of the Chemical Society in succession to Mr. A. Vernon Harcourt, M.A., M.D., D.C.L., F.R.S.:—

Baly, E. C. C.; Baker, C. F.; Burgess, Herbert E.; Blount, Bertram; Blundstone, Edward R.; Berncastle, Richard; Cassal, Charles E.; Chattaway, F. D.; Chapman, Alfred C.; Collie, J. Norman; Chorley, John C.; Coste, J. H.; Crossley, Arthur; Dufton, S. T.; Ekins, Arthur E.; Edwards, W. Buckland; Evans, R. C. T.; Elborne, William; Earl, Alfred; Elford, P.; Forster, M. O.; Graham, Edward; Grimwood, R.; Harley, Vaughan; Harvey, Sydney; Baker, Julian L.;

Floris, R. B.; Jackman, E. J.; Jones, Cecil; Johnson, David; Kipping, Stanley F.; Kellas, Alex. M.; Kingzett, C. T.; Ling, A.; Lapworth, A.; Livingston, W. T.; Littlefield, R. D.; Routledge, R.; Lamb, Edmund; Moody, Gerald T.; Bodmer, R.; Moor, C. G.; Millar, J. H.; McCrae, J.; Macdonald, G.; Mills, Charles; McGowan, Geo.; Pope, W. J.; Parry, Ernest J.; Picton, Harold; Plimpton, R. T.; Richmond, H. Droop; Simpson, Arthur M.; Stevens, H. P.; Travers, M. W.; Le Sueur, H. R.; Wade, John; Wagner, W. G.; Wilsmore, N. T. M.; Walker, J. Wallace; Sworn, Sydney A.; Cornish, Vaughan; Sykes, Walter J.; Waterhouse, Robert; Chattaway, William; Priest, Martin; Marsh, J. E.; Muspratt, Edmund K.; Mitchell, C. A.; Muspratt, Sydney K.; Adams, Arthur; Marshall, Arthur; Wilson, John; Bone, W. A.; Fisher, E. H.; Chapman, Arthur J.; Wheelwright, E. W.; Lewis, W. H.; Sudborough, J. J.; Veley, V. H.; Walker, James; Colman, Harold, G.; Christopher, George; Macnair, D. S.; Bell, Chichester A.; Wertheimer, J.; Hodgkin, John; Archbutt, Leonard; Muir, M. M. Pattison; Shaw, G. E.; Taylor, R. L.; Colwell, J. Kear; Cribb, Cecil H.; Butterfield, W. J. Atkinson; Hanes, Edgar S.: Sutherland, D. A.; Teed, Frank L.; Fulcher, L. W.; Heller, W. M.; Sandford, P. Gerald; Snape, H. Lloyd; Knight, J. B.; Cooper, A. J.; Adams, P. T.; Adams, M. A.; Eiloart, A.; Corfield, W. H.; Muter, J.; Muter, A. H. M.; Dodd, W. H.; Koningh, L. de; Mawer, W. F.; Lascelles, P. B.; Bruce, James; Turpin, G. S.

Professor Collie stated that the nomination of Professor Ramsay had been made without his knowledge or his permission.

Of the following papers, those marked * were read.

***44. "On the atomic weight of carbon." By Alexander Scott, M.A., D.Sc.**

The object of this paper is to call attention to the unsatisfactory nature of the experimental evidence on which the determinations of the atomic weight of carbon rest. The two methods on which reliance is chiefly placed are shown to be only in agreement because a source of error which affects both acts in opposite directions. This is due to an erroneous determination of Dumas and Stas, in 1840, of the expansion produced in potash solutions by the absorption of carbon dioxide. All later workers at this problem seem to have accepted their conclusions without further verification. The seriousness of this source of error is apparent when we consider that over 40 milligrams is the correction for the weight *in vacuo* of the carbon dioxide in one experiment

alone. The correction per gram of carbon dioxide is shown to be 0·56 to 0·57 c.c., instead of 0·15 c.c., as taken by Dumas and Stas. The probable effect of the gases "occluded" in the copper oxide is next considered, and, as far as possible, allowed for. It is shown by many determinations that the experiments of Richards give the quantity as much too great, the mean result of his best experiments being 0·088 per cent. by weight of nitrogen in copper oxide made from the nitrate, whilst the experiments here described give as a mean only about 0·007 per cent.

Other sources of error and the best methods of making more accurate determinations are next considered. The recalculated values are 12·008 from the combustion of the various forms of carbon, and 12·050 from the conversion of the monoxide into the dioxide.

Discussion.

In reply to questions from Mr. Groves, Mr. Blount, Mr. Heycock, and the President, Dr. Scott stated that 150 grams of the oxalate furnished about 4 grams of carbon. In the case of the potash solution, it was the expansion of the liquid which had to be corrected for. The rate of absorption of carbon dioxide by potash solution at any given time was affected by the amount of carbon dioxide which had been already absorbed. Carbon monoxide was completely absorbed by potash after some time.

*45. "On a new series of mixed sulphates of the vitriol group." By Alexander Scott, M.A., D.Sc.

This paper describes a new series of mixed sulphates of the form $(M,N)''SO_4,H_2O$. The most interesting is the ferrous cupric sulphate, the colour of which is reddish-brown; it dissolves in water, giving a blue-green solution.

The composition of this salt on analysis corresponds to the formula $(CuFe)SO_4,H_2O$, or $(Fe_5Cu_2)(SO_4)_7,7H_2O$. These salts are made by adding about an equal bulk of strong sulphuric acid to solutions of the mixed sulphates.

Discussion.

Mr. Spiller, referring to investigations he had conducted on some double sulphates of this group, crystallised from water, the results of which were communicated to the British Association ten years ago, said that he was led to the conclusion that the amount of water of crystallisation in such mixed sulphates was the mean of that present in their constituent salts.

***46. "A synthesis of camphoronic acid." By William Henry Perkin, jun., F.R.S., and Jocelyn Field Thorpe, Ph.D.**

In a previous communication (Proc., 1896, **12**, 155) experiments were described dealing with the action of metallic zinc on mixtures of bromo-ethylic salts and ketones or ketonic acids; notably on mixtures of ethylic aceto-acetate and ethylic α-brom-iso-butyrate, and of ethylic dimethylacetoacetate and ethylic bromoacetate, and it was shown that the same hydroxy-ethylic salt, namely, ethylic-β-hydroxy-α-α-β-trimethyl glutarate was in each case produced thus:

$$\begin{matrix} Me_2{:}CBr \\ | \\ EtOOC \end{matrix} + \begin{matrix} CO\cdot CH_2 \\ | \\ CH_3COOEt \end{matrix} \quad \text{and} \quad \begin{matrix} Me_2{:}C\cdot C \\ | \quad | \\ EtOOC\ CH_3 \end{matrix} + \begin{matrix} CH_2Br \\ | \\ COOEt \end{matrix}$$

give

$$\begin{matrix} Me_2{:}C\cdot C(OH)\cdot CH_2 \\ | \quad | \quad | \\ EtOOC\ CH_3 \quad COOEt \end{matrix}$$

This *ethylic-β-hydroxy-α-α-β-trimethylglutarate* (b. p. 165°, 30 mm.), as previously stated, splits up, on hydrolysis with alcoholic potash, into acetic and isobutyric acids. When, however, it is boiled with dilute hydrochloric acid, it does not behave in this way, but yields considerable quantities of the corresponding *β-hydroxy-α-α-β-trimethylglutaric acid*, $COOH\cdot C(CH_3)_2\cdot C(OH)\cdot(CH_3)\cdot CH_2\cdot COOH$, which is a crystalline body, separating from a mixture of light petroleum and ethylic acetate in glistening prisms melting at 128°.

In the previous communication, an acid melting at 148°, obtained by the action of alcoholic potassium cyanide on ethylic-β-brom-α-α-β-trimethyl glutarate, was described as a trimethylglutaric acid: we now wish to correct this statement. Alcoholic potassium cyanide is apparently without action upon the bromethylic salt at the temperature of the boiling water bath, and, on hydrolysing the product with alcoholic potassium hydroxide, the unsaturated acid, *α-α-β-trimethylglutaconic acid*, $COOH\cdot CH{:}C(CH_3)\cdot C(CH_3)_2COOH$, melting at 148°, is produced, and not the trimethylglutaric acid as was at first supposed. This acid is remarkably stable, and is not affected by boiling with sodium amalgam. When, however, its boiling solution in alcohol is treated with sodium, the unsaturated acid is gradually reduced to *α-α-β-trimethylglutaric acid*, $COOH\cdot CH_2\cdot CH(CH_3)\cdot C(CH_3)_2\cdot COOH$, which crystallises from dilute hydrochloric acid in prismatic needles melting at 109°; the anhydride of this acid melts at 38°, and yields, on treatment with aniline, an *anilic acid* forming lustrous plates from dilute alcohol melting at 155°. Although the melting points of the acid and of the anil are very similar to those of the trimethylglutaric acid which Balbiano

obtained from camphoric acid, it does not appear that the acids are identical, and it is probable that Balbiano's acid is the isomeric *α-β-β*-trimethylglutaric acid, $COOH \cdot CH(CH_3) \cdot C(CH_3)_2 \cdot CH_2 \cdot COOH$, as this chemist suggests.

On treating ethylic *β*-hydroxy-*α-α-β*-trimethylglutarate with phosphorus pentachloride, the chlorethylic salt, namely, *β-chlor-αα-β-trimethyl glutarate*, $COOC_2H_5C(CH_3)_2 \cdot C(Cl) \cdot (CH_3) \cdot CH_2 \cdot COOC_2H_5$, is obtained as a colourless, mobile liquid which boils at 139° (20 mm.). When this substance or the corresponding bromo-derivative is heated with alcoholic potassium cyanide in a closed tube at 160° *ethylic β-cyano-α-α-trimethyl glutarate*, $COOEt \cdot C(Me_2) \cdot C \cdot (CN) \cdot (Me) \cdot CH_2 \cdot COOEt$, is obtained after twelve hours as an oily liquid boiling at 180—185° (25 mm.). It is difficult to isolate in the pure condition owing to the presence of varying quantities of the ethylic salt of trimethylglutaconic acid, a substance which boils at about the same temperature as the nitrile (175°. 30 mm.).

This nitrile was hydrolysed by boiling with dilute hydrochloric acid, and after filtering from the trimethylglutaconic acid, which separated on cooling, the filtrate yielded on neutralisation with ammonia and addition of barium chloride no precipitate, but on boiling, a quantity of a sparingly soluble barium salt separated. This salt was collected, well washed, and decomposed by boiling with the calculated quantity of sulphuric acid; the filtrate from the barium sulphate was then evaporated to a small bulk, when on cooling a crystalline acid separated, which melted at 157° with decomposition, and on analysis gave the following numbers:—

0·1258 gram gave 0·2276 gram CO_2 and 0·0746 gram H_2O. Calc. for $(C_9H_{14}O_6)$: H = 6·40; C = 49·50. Found: H = 6·58; C = 49·34. *α-α-β-trimethyltricarballylic acid*, $COOH \cdot CH_2C(COOH)(Me)C(Me_2)COOH$.

That this acid is identical with camphoronic acid is, in our opinion, proved by the following considerations:—

(1) The synthetical acid gives the same results on analysis, and melts at the same temperature as camphoronic acid.

(2) When equal quantities of the synthetical acid and camphoronic acid are intimately mixed, the mixture melts at exactly the same temperature, *i.e.*, 157°, with decomposition.

(3) It gives, when dissolved in a slight excess of ammonia, no precipitate with barium chloride until the liquid is warmed, and then the insoluble barium salt separates exactly as in the case of camphoronic acid.

(4) When heated with acetyl chloride, both the acids are converted into an anhydro-acid, which melts in both cases at 135—136°.

The anhydrocamphoronic acid from the synthetical acid gave on analysis the following results. Found, C = 54·03; H = 6·11. $C_9H_{12}O_5$ Calc. C = 54·00; H = 6·00 per cent.

In a previous communication (Proc., 1896, 12, 192),* one of us had occasion to express the opinion that Tiemann's formula for camphoronic acid, $COOH \cdot CH(CH_3) \cdot C(CH_3)_2 \cdot CH \cdot (COOH)_2$, which contains the group $-CH(COOH)_2$ must be incorrect, on account of the fact that camphoronic acid, when heated with water at 230°, is not decomposed with elimination of CO_2. The experiments which we have briefly described in this communication appear to us to prove that camphoronic acid has the constitution first proposed by Bredt (*Ber.*, 1893, **26**, 3048), namely, that of an $\alpha\alpha\beta$-trimethyltricarballylic acid,

$$COOH \cdot C(CH_3)_2 \cdot CCH_3(COOH) \cdot CH_2 \cdot COOH.$$

47. "Note on a method for determining melting points." By Ernest H. Cook, D.Sc.

So many methods have been introduced for the determination of melting points, that an apology is perhaps necessary for describing another, but the following method has been found to work so well in this laboratory, and to be so easy of manipulation, that the author ventures to place it on record.

Notwithstanding, however, the theoretical simplicity of taking a melting point, it is surprising that in commercial work considerable differences frequently occur between analysts when reporting upon such a substance, for example, as paraffin scale. Probably most, if not all, of these differences are caused by the different methods employed. Thus it is well known that "the English test," which consists in allowing the wax to solidify in a test-tube in which the thermometer is placed gives results from $2\frac{1}{2}$ to 3 degrees Fahr. lower than the "American test," in which the wax is melted in an open dish. Both these methods again differ slightly from the capillary-tube plan, and in this process a different result is obtained when an open tube is used than when it is closed. There are in fact many precautions which are necessary to be observed if concordant results are to be obtained, and it is much to be desired that some distinct and definite regulations should be made with reference to the matter.

The apparatus employed is a beaker filled to the brim with water; inside this, and separated from it on all sides, is a smaller one. The smaller beaker is partly filled with mercury in which is placed a thermometer. A stirrer is used to keep the water in the large beaker of uniform temperature. A cardboard or other disc covers the smaller beaker when the operation is in progress. The whole is heated from below by means of a sand bath. When the melting point to be deter-

* The formula given here from Bredt's constitution of camphoronic acid is a misprint, it should be $COOH \cdot C(CH_3)_2—C(CH_3)(COOH)—CH_2 \cdot COOH$.

mined is under 30° it is better to replace the sand bath by an evaporating dish containing water.

The process is conducted as follows. The material whose melting point is to be taken is placed on three or four small pieces of thin ferro-type plate or other thin metallic sheet, or on the cover glasses which are used for microscope slides. If ferro-type or other metallic slips are used, care must be taken to remove the varnish or other coating in order that good metallic contact can be had with the mercury. The slips, with the substance on them, are now placed on the surface of the mercury and the heat applied until the substance melts. The solidifying point is obtained by raising the temperature above the melting point and allowing the beaker to cool, noting the thermometer when the first solidification takes place.

For temperatures between 100° and 200°, the larger beaker is filled with paraffin wax.

The following precautions have been found to be necessary:—(1) The temperature must be made to rise very slowly. (2) The liquid in the outer beaker must be frequently stirred. (3) Not less than 2·5 cm. in depth of mercury must cover the inner beaker. (4) Sufficient volume of water must be allowed between the two beakers. The minimum distances to give good results are 1 in. between them laterally and $1\frac{1}{2}$ inch at the bottom. (5) The inner beaker must be immersed a sufficient depth in the water. This point is of great importance, the least distance between the top of the mercury and the top of the water being 3 inches. A greater distance is, however, to be preferred. (6) The whole apparatus should be protected from draughts. (7) The disc should be kept on the smaller beaker during the determination.

The following examples will show the degree of accuracy to be obtained in ordinary working, some of the results being obtained by students who have never taken a melting point determination before. Paraffin wax (1), 49·8, 49·7, 49·5, 49·8. Paraffin wax (2), 46·2, 46·0, 46·0, 46·0. Paraffin wax (3), 46·5, 46·3, 46·5. Ortho-mono-nitro-phenol 44·5, 44·7. Urea, 131·0, 131·5, 131·2.

48. "Velocity of urea formation in aqueous alcohol." By James Walker, D.Sc., and Sydney A. Kay, B.Sc.

The authors have investigated the rate of formation of urea from ammonium cyanate in pure water, and in mixtures of water and alcohol containing 10, 30, 50, 70, and 90 per cent. by volume of the latter. The alcohol acts in two ways: first, it diminishes the degree of dissociation of the cyanate and thus retards the action by diminishing the number of active molecules; secondly, it increases the rate at which the ions produced by the dissociation interact. The

second mode of action outweighs the first, so that there is on the whole a marked acceleration as the water of the solvent is replaced by alcohol. If the reverse transformation of urea into cyanate, and the degree of dissociation of the latter at the various stages of the process, are taken into consideration, the requirements of the law of mass-action are strictly fulfilled.

Methylic alcohol, acetone, glycol, glycerol, and cane-sugar exert a similar accelerating effect when part of the water used as solvent is replaced by them.

From the displacement of the point of equilibrium between cyanate and urea by change of temperature, it is calculated that the transformation of ammonium ions and cyanic ions into urea is accompanied by a heat evolution of about 5,000 cal. per gram-molecule.

49. "Action of alkyl haloids on aldoximes and ketoximes." By Wyndham R. Dunstan, F.R.S., and Ernest Goulding.

The authors find that, when formaldoxime, acetaldoxime, and acetoxime are heated in alcoholic solution with an alkyl iodide or bromide, they are converted into compounds of alkyloximes in which the alkyl group is united to nitrogen $R'CHN(R')O$ and $R'_2CNCH(R')O$. These derivatives are isomerides of the little known ethers of the oximes $R'CH:NOR'$ and R'_2CNOR', and are to be regarded as derivatives of the tautomeric or isoximido-forms of the ordinary aldoxime or ketoxime $R'CHNH$ and R'_2CNH in which the alkyl replaces the hydrogen of the amido-group. Their constitution has been proved by their hydrolysis into β-substituted hydroxylamines, $NH(R')OH$, and the corresponding aldehyde or ketone.

Formaldoxime, when mixed with methyliodide, either in alcoholic or ethereal solution, is converted into a crystalline salt of the formula $(CH_2NOH)_3CH_3I$. It has been previously shown (Dunstan and Bossi, Proc., 1894, 10, 55) that formaldoxime forms salts with monobasic acids which contain three molecules of the oxime, $(CH_2NOH)_3HCl$, &c. On hydrolysis, followed by reduction, one molecule of methylamine hydrochloride and two of ammonium chloride are produced, and on heating near its melting point (102°) only two molecules of formaldoxime distil from it. The formula of the compound may therefore be written $(CH_2NOH)_2,CH_2N(CH_3)O.HI$. The base corresponding with this salt could not be separated. Methyl bromide heated with formaldoxime furnishes the corresponding hydrobromide.

Acetaldoxime combines with methyl iodide, forming the hydriodide of a base which has so far only been obtained in the liquid state even

after a process of fractional precipitation of an alcoholic solution by ether. On hydrolysis, this salt furnishes acetaldehyde and β-methylhydroxylamine. There can, therefore, be no doubt that its formula is $CH_3CHN(CH_3)O.HI$. Methyl bromide combines in the same manner, forming the corresponding hydrobromide. Ethyl iodide forms the hydriodide of the ethyl derivative, $CH_3CHN(C_2H_5)O.HI$. Neither of the salts has been crystallised and the corresponding bases are highly unstable.

Acetoxime.—By heating acetoxime with methyl iodide, a red liquid is obtained which, on concentration, deposits red crystals with a fine green lustre. The mother liquor furnished the little-known *methylamine hydriodide* ($CH_3NH_2.HI$) in glistening, crystalline plates (from alcohol-and ether). This is a very stable non-deliquescent salt, melting at 220° with partial decomposition.

The red crystals were proved by analysis to be a methylacetoxime periodide of the formula $[(CH_3)_2CN(CH_3)O.HI]_2I$. On hydrolysis, it breaks up into acetone and β-methylhydroxylamine.

Many attempts were made to isolate the hydriodide from the periodide, and also to prepare other salts from this compound, including the base, but without success, owing to the great instability of these substances.

The hydrobromide appears to be formed when methyl bromide is heated with an alcoholic solution of acetoxime, but this salt could not be crystallised.

PASTEUR MEMORIAL LECTURE.

The Pasteur Memorial Lecture will be delivered by Professor Percy Frankland, Ph.D., F.R.S., at an extra meeting of the Society on Thursday, March 25th, at 8 p.m.

ANNIVERSARY MEETING.

The Anniversary Meeting will be held on Wednesday, March 31st, at 3 o'clock in the afternoon.

ANNIVERSARY DINNER.

It has been arranged that the Fellows of the Society and their friends shall dine together at the Criterion Restaurant on Wednesday, March 31st, at 7 p.m. The President, Mr. A. G. Vernon Harcourt, in

the Chair. *The Secretaries will be glad to receive notification from those Fellows who intend to be present before Friday, March 26th, so that the final arrangements may be completed.*

At the Meeting on April 1st, the following Paper will be received. The authors have announced their intention of being present.

"On the oxidation of α-γ-dimethyl-α′-chloropyridine." By E. Aston and J. Norman Collie, Ph.D., F.R.S.

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PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

EDITED BY THE SECRETARIES.

No. 178. Session 1896–7.

March 25th, 1897. Extra Meeting. Mr. A. G. VERNON HARCOURT President, in the chair.

Professor P. FRANKLAND, Ph.D., B.Sc., F.R.S., delivered the Pasteur Memorial Lecture.

It was pointed out that, although the name of Pasteur was associated with the progress of so many branches of science, it appeared that his remarkable success in such varied fields of investigation was in large measure due to the chemical discipline under which he had grown up, and in his having almost for the first time extended the experimental methods and close reasoning of the chemist to other sciences, in which previous investigators had been mostly occupied with matters of a superficial character. Reference was then made to Pasteur's birth, on December 27, 1822, his early life and entrance as a student into the École Normale, to his being retained as an assistant there by Balard, and to his interest being awakened in the study of crystallography by Delafosse. His classical researches on the tartrates and malates were then described, and the principal results discussed from a practical and theoretical point of view. It was shown of what enormous importance for the development of chemical theory had been the introduction by Pasteur of the conception of molecular symmetry and dissymmetry, whilst the wide applicability of his methods of investigating stereoisomeric compounds was indicated in outline. The manner in which he was next led to investigate fermentation phenomena was then described, his conflict with Liebig was touched upon, and his overthrow of the so-called 'chemical fermentation theory' detailed. Reference was then made to his participation in the spontaneous generation controversy, and to his victories over Pouchet, Joly, Musset, and Bastian, the last champions of the doctrine of abiogenesis. The practical aspects of Pasteur's fermentation studies

were briefly considered, the famous 'Études sur la bière'; 'sur le vin,' and 'sur le vinaigre,' as well as process known as *pasteurisation*. The direct influence of these fermentation studies on medicine, surgery, and public health was pointed out, and the manner in which they had led to the magnificent work of Lister on the antiseptic treatment of wounds was indicated. Pasteur's investigation of the destructive silkworm diseases, *pébrine* and *flacherie*, was then dealt with, and his gradual attraction into the field of pathological research traced. His studies on anthrax, his recognition of the bacillus of malignant œdema, and his discovery of the *staphylococcus pyogenes* and of the *streptococcus pyogenes* were referred to. Then the manner in which he came upon the possibility of attenuating viruses and preparing vaccines was described; the lecture concluding with an account of the methods of protective inoculation devised by Pasteur, first for fowl-cholera, then for anthrax, for swine-measles, and his final triumph in successfully elaborating a curative treatment for rabies.

Lord Lister, P.R.S., proposed, and Sir Henry Roscoe seconded, a vote of thanks to Professor Percy Frankland, which was carried unanimously.

March 31st, 1896. Anniversary Meeting. Mr. A. G. Vernon Harcourt, President, in the Chair.

Professor Collie, F.R.S., and Dr. Wynne, F.R.S., were appointed Scrutators, and a ballot was opened for the election of Officers and Council for the ensuing year, the ballot being closed at the conclusion of the President's address.

The Longstaff Medal was then presented to Professor Ramsay for the discovery of helium, and for his share in the investigation of argon. The President referred to the circumstances under which the first announcement of the discovery was made, and expressed the pleasure he felt in presenting him with the Medal.

The President began his address by thanking the Fellows, and more especially the Officers and Council, for the kindness with which they had aided him during his year of office, and expressed his pleasure at the progress of the Society during the past year. He referred to the arrangements made for the reading of papers, and suggested means by which the discussions might be made more useful.

The publication of the Jubilee volume, largely drawn up by Dr. Armstrong, was mentioned, and the services rendered by Mr. Warington

in its preparation were acknowledged. The Hofmann Memorial Lectures had also been issued. Lothar Meyer and Pasteur Memorial Lectures had been delivered in the year, and arrangements had been made for the Kekulé Lecture. Reference was also made to the work of the Council through the year, to the death of Sir William Grove, an original member of the Society, and to the munificent donation of one thousand guineas by Mr. J. J. Tustin.

The remainder of the address was devoted to a consideration of the question whether the changes which matter undergoes are different in their nature.

The numerical strength of the Society was as follows :—

Number of Fellows, March 31st, 1896		2,019
„ „ since elected		130
„ „ reinstated by Council		7
		2,156
Removed on account of non-payment of two annual subscriptions	25	
Withdrawn	29	
Deaths	23	77
Number of Fellows, March 31st, 1897		2,079
Foreign Members		27

The names of those removed were :—P. T. Adams ; Hugh Barclay ; Thos. Cockerill ; Thos. Chambers ; S. M. Copeman ; C. A. Heywood ; John Holliday ; A. P. Hope ; J. J. Howitt ; J. R. Kaye ; L. R. Lenox ; O. A. B. Lowman ; J. G. Mactaggart ; H. J. Monson ; F. C. Moorwood ; Percy Morton ; Ivan Shopoff ; E. H. Smith ; T. B. Stillman ; C. A. Stitt ; Prof. Tanner ; G. de R. Thompson ; F. W. Westaway ; W. A. Whiston ; D. Wilkinson.

The following have withdrawn :—F. T. Bond ; T. Coomber ; C. L. Field ; A. E. Fletcher ; C. C. Grundy ; E. C. Henning ; G. S. Johnson ; W. H. Joseland ; C. J. Leaper ; J. H. Maiden ; J. W. Marshall ; John Morrison ; H. W. Morrow ; J. A. Nettleton ; J. C. Oman ; C. S. du R. Preller ; Lawrence Priestley ; H. H. Robjohns ; H. C. Sacré ; W. S. Saunders ; V. P. Sells ; R. de F. Shepherd ; R. Stockdale ; Frederick Tetley ; J. C. Thresh ; A. H. Turton ; Geo. Watson ; F. Whiteley ; C. Willmore.

The following have died :—I. M. T. Anderson ; John Curragh ; Captain Marshall Hall ; G. Harley, F.R.S. ; James Hart ; John Hughes ; W. Lapraik, Ph.D. ; J. B. L. Mackay ; A. H. Mason ; H. A. Nott ; Baron F. von Mueller, F.R.S. ; W. J. Palmer ; Sir J.

Prestwich, F.R.S.; Edward Rawlins; G. F. Schacht; James Scorgie; T. Shimidzu; T. J. Smith; Charles Tomlinson, F.R.S.; W. H. Walenn; Richard Weaver; W. H. Wood; T. G. Wormley, M.D.

The number of communications made to the Society during the year was 173.

One hundred and seventeen papers and 3 Memorial Lectures were published in the Transactions for 1896, occupying 1702 pages, whereas in the preceding year 116 papers were published, occupying 1172 pages.

The following were the statistics relating to the Abstracts.

	Pages.	No. of Abstracts.
PART I.		
Organic Chemistry	716	1201
PART II.		
General and Physical Chemistry		319
Inorganic Chemistry		287
Mineralogical Chemistry		267
Physiological Chemistry		182
Chemistry of Vegetable Physiology and Agriculture		153
Analytical Chemistry		430
Total in Part II	684	1638
Total in Parts I and II	1400	2839

Eight hundred and fifteen volumes had been borrowed from, and 163 books, 310 volumes of periodicals, and 24 pamphlets added to the Library.

Professor ODLING, F.R.S., proposed a vote of thanks to the President, coupled with the request that he would allow his address to be printed in the Transactions.

Dr. FRANKLAND, F.R.S., seconded the motion, which was carried by acclamation.

The PRESIDENT having returned thanks,

Dr. THORPE, F.R.S., the treasurer, gave an account of the balance sheet, which he laid before the Society, duly audited.

The receipts had been:—By admission fees and subscriptions, £4134; by sale of Journal and advertisements, £702 14*s.* 9*d.*; and by dividends on invested capital, £415 10*s.* 6*d.* The expenses had been:—On account of the Journal, £3089 8*s.* 1*d.*; on account of the

Proceedings, £237 18*s.* 1*d.*; on account of the General Index, £464 3*s.* 9*d.*; on account of the Library, £355 2*s.* 0*d.*; on account of the Jubilee, £336 12*s.* 1*d.*; House expenses £199 17*s.* 4*d.*; the total expenditure being £5385 4*s.* 7*d.* Grants amounting to £308 had been made to Fellows from the Research Fund during the year.

Sir F. Abel, F.R.S., proposed that the thanks of the Fellows be tendered to the Treasurer for his services during the past year; this motion was seconded by Mr. Phipson Beale, Q.C., and carried.

The Treasurer, in responding, proposed a vote of thanks to the auditors.

Mr. J. H. M. Page seconded the motion, which was unanimously adopted, and acknowledged by Mr. H. B. Baker.

Dr. W. J. Russell, F.R.S., proposed a vote of thanks to the Officers and Council.

Professor Tilden, F.R.S., seconded the motion, which was unanimously adopted.

Dr. Dyer responded on behalf of the Council.

Professor H. B. Dixon, F.R.S., proposed a vote of thanks to the Editor, Sub-Editor, Abstractors, and Indexers, which was seconded by Mr. Friswell and carried.

Mr. Groves, F.R.S., responded.

The Scrutators having presented their report to the President, he declared that the following had been duly elected:—

President: James Dewar, M.A., LL.D., F.R.S.

Vice-Presidents who have filled the office of President: Sir F. A. Abel, Bart., K.C.B., D.C.L., F.R.S.; H. E. Armstrong, Ph.D., LL.D., F.R.S.; A. Crum Brown, D.Sc., M.D., F.R.S.; W. Crookes, F.R.S.; E. Frankland, D.C.L., F.R.S.; Sir J. H. Gilbert, Ph.D., F.R.S.; J. H. Gladstone, Ph.D., F.R.S.; A. Vernon Harcourt, D.C.L., F.R.S.; H. Müller, Ph.D., F.R.S.; W. Odling, M.B., F.R.S.; W. H. Perkin, LL.D., Ph.D., F.R.S.; Lord Playfair, Ph.D., K.C.B., F.R.S.; Sir H. E. Roscoe, LL.D., F.R.S.; W. J. Russell, Ph.D. F.R.S.; A. W. Williamson, LL.D., F.R.S.

Vice-Presidents: Francis Robert Japp, M.A., Ph.D., LL.D., F.R.S.; Ludwig Mond, F.R.S.; William Ramsay, Ph.D., F.R.S.; J. Emerson Reynolds, D.Sc., F.R.S.; W. Chandler Roberts-Austen, C.B., F.R.S.; William A. Tilden, F.R.S.

Secretaries: J. Millar Thomson; Wyndham R. Dunstan, M.A., F.R.S.

Foreign Secretary: Raphael Meldola, F.R.S.

Treasurer: T. E. Thorpe, LL.D., F.R.S.

Other Members of Council: P. Phillips Bedson, D.Sc.; Bennett Hooper Brough; Otto Hehner; C. T. Heycock, M.A., F.R.S.;

Herbert McLeod, F.R.S.; Rudolph Messel, Ph.D.; H. Forster Morley, M.A.; James Wyllie Rodger; T. Kirke Rose, D.Sc.; Alexander Scott, M.A., D.Sc.; Arthur Smithells, B.Sc.; Sydney Young, D.Sc., F.R.S.

The question having been raised as to whether the number of votes cast for each candidate for the Presidency should be declared, the PRESIDENT stated that this had not been the custom, but he would take the sense of the meeting on the point. A majority being in favour of a declaration of the numbers, the PRESIDENT conferred with the Scrutators and then stated that there was a difficulty in announcing the numbers, owing to a question having arisen in reference to the validity of certain voting papers, in which the instruction to erase the printed name had not been complied with.

Inasmuch as the rejection of these irregular papers would only increase the majority and not affect the result of the election, and as it now appeared that the announcement of the numbers would involve recounting the votes, the PRESIDENT suggested that the Fellows should be content with the Scrutators' report. The ruling of the President as to the validity of the irregular papers having been requested, he stated that, in his opinion, they were invalid.

Questions having been asked as to the bye-laws governing the election, the PRESIDENT stated that the election had been conducted in strict accordance with the bye-laws, and he therefore declared the election valid.

In the evening, at 7 p.m., the Fellows and their friends dined together at the Criterion Restaurant, Mr. A. G. Vernon Harcourt, the retiring President, in the Chair.

The following Fellows and guests were present.

Alexander, Mr.
Armstrong, Dr., F.R.S.
Atkinson, Dr. E.
Barlet, Mr.
Bauerman, Mr. H.
Bayly, Mr.
Bevan, Mr. E. J.
Bidwell, Mr. Shelford, F.R.S., *President of the Physical Society.*
Blundstone, Mr.
Blundstone, Mr. S. R.
Brough, Mr
Brown, Mr. H., F.R.S.
Burbridge, Mr.
Butterfield, Mr.
Candy, Mr.
Carr, Mr. F. H.
Carteighe, Mr.
Chattaway, Dr.
Chevalier, R.N., Com.
Christie, Mr., F.R.S., *Astronomer Royal.*
Clerk, Mr. Dugald
Clowes, Prof.
Cooper, Mr. A. B.
Cooper, Mr.
Cowper-Coles, Mr.
Crookes, Mr. W., F.R.S.
Crookes, Mr. H.
Cross, Mr. C. F.
Crossley, Dr.

Daoust, Mr.
Dewar, Prof., F.R.S. (*President Elect*).
Dixon, Prof., F.R.S.
Dodds, Mr. J. M.
Douglas, Mr. W.
Dunstan, Prof., F.R.S., *Hon. Secretary.*
Dyer, Dr. B., *President of the Society of Public Analysts.*

Elder, Mr. H. M., *Secretary of the Physical Society.*
Evans, Mr. R. C.
Evans, Sir John, K.C.B., *Treas. R.S.*
Ewan, Dr.

Fairley, Mr. T.
Fenton, Mr.
Fitzroy, Col.
Formoy, Mr.
Forster, Dr.
Foster, Prof. G. C., F.R.S.
Foster, Prof. M., *Secretary R.S.*

Gardiner, Dr. H. S.
Gladstone, Dr., F.R.S.
Goodwin, Mr. H. B.
Griffiths, Mr. E. H., F.R.S.
Gordon, Mr. J. G.
Greenaway, Mr.
Groves, Mr., F.R.S.

Hall, Mr. S.
Hall, Mr. S. G.
Hammick, Mr. J. F.
Harcourt, Mr. A. G. V., F.R.S.
Hare, Mr. A. T.
Harvey, Dr.
Hehner, Mr.
Heycock, Mr. C. T., F.R.S.
Hicks, Dr., F.R.S., *President of the Geological Society.*
Hills, Capt., R.E.
Hills, Mr. W., *Pres. of the Pharm. Soc.*
Howard, Mr. D. Lloyd.
Huntington, Prof.
Huntly, Mr. G. N.

Jackson, Mr. H.
Jenks, Mr. R. L.
Jones, Mr. G. F.

Kellner, Dr.
Kemp, Mr. W. J.
Kirkaldy, Mr.
Knowles, Mr. J.

Lawson, Dr.
Lister, Lord, P.R.S.
Lloyd, Gen., C.B.

MacEwan, Mr.
MacMahon, Major, R.A., F.R.S.
Mallet, Mr. F. R.

Martin, Mr. W. H.
Martindale, Mr.
Messel, Dr., *Chairman of the London Section Society Chemical Industry.*
Masters, Mr. W.
Matthey, Mr. E.
McLeod, Prof., F.R.S.
Meldola, Prof., F.R.S., *Foreign Secretary.*
Moody, Dr.
Morris, Dr. G. H.
Morrison, Mr. C. R.
Mortimer, Capt.
Moss, Mr. R. J.
Moulton, Mr. Fletcher, Q.C., F.R.S.
Müller, Dr. H., F.R.S.

Nagel, Mr.
Neville, Mr.

Obach, Dr.
Odling, Prof., F.R.S.
Orange, Dr., C.B.
Ormsby, Col., R.A.

Page, Mr.
Pearce, Mr.
Perkin, Dr., F.R.S., *Master of the Leather-sellers' Company.*
Ping, Mr.
Pope, Dr.
Power, Dr. F. B.
Pritchard, Prof.

Rée. Dr.
Reynolds, Prof. Emerson, F.R.S.
Robbins, Mr.
Roberts-Austen, Prof., C.B., F.R.S.
Rose, Dr.
Rosenblum, Mr.
Rücker, Prof., F.R.S., *Sec. R.S.*
Russell, Dr. W. J., F.R.S.

Scott, Dr.
Seaton, Dr.
Siemens, Mr. A.
Slater, Mr.
Spooner, Mr. F. B.
Sprengel, Prof., F.R.S.
Steele, Mr. R., *Assistant Secretary and Librarian.*
Stevenson, Dr., *President Institute of Chemistry.*
Sudlow, Mr.
Sutherland, Mr. D. A.

Taubman, Mr. R.
Thomson, Prof. J. M., *Honorary Secretary.*
Thorpe, Prof., F.R.S., *Treasurer.*
Tilden, Prof., F.R.S.,
Tookey, Mr.
Turner, Mr.
Tutton, Mr.

Vautin, Mr.
Voelcker, Dr. J. A.

Wade, Mr. J.
Wellcome, Mr. H. S.
Whitaker, Mr., F.R.S.
Williamson, Dr. S.
Wynne, Dr., F.R.S.

The following toasts were proposed.

By the Chairman.

1. Her Most Gracious Majesty the Queen.
2. Their Royal Highnesses the Prince and Princess of Wales and the other members of the Royal Family.

By the Right Hon. Lord Lister, President of the Royal Society.

3. Prosperity to the Chemical Society.

By William Crookes, Esq., F.R.S.

4. The Learned and Scientific Societies, coupled with the name of Sir John Evans, K.C.B., Treasurer of the Royal Society.

By Dr. J. H. Gladstone, F.R.S.

5. The Guests, coupled with the name of Professor Michael Foster, Secretary of the Royal Society.

By Dr. W. J. Russell, F.R.S.

6. The retiring President.

By Dr. Armstrong, F.R.S.

7. The Secretaries, coupled with the name of Professor J. M. Thomson.

April 1st, 1897. Professor Dewar, F.R.S., President, in the Chair.

Messrs. William Douglas, Ernest Goulding, T. H. Lee and W. A. Davis were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. William Barlow, Hillfield, Muswell Hill, N.; James Brierley, 12 Brunswick Square, Southampton; Alexander Duckham, Crooms Hill, Greenwich Park, S.E.; Harold William Harrie, 298 Amhurst Road, Stoke Newington, N.; Sydney Hill, 11 Salisbury Street, Hull; Willie Lee Mallinson, Gawthorp Green, Kirkheaton; Edmund Howd Miller, M.A., Ph.D., Columbia University, U.S.A.; Joseph Previte Kennedy Orton, B.A., Ph.D., 20 Loughborough Road, Brixton, S.W.; Charles Alfred West, 105 Sydney Street, Chelsea, S.W.; Paul Thomas White, Horton Field, West Drayton.

Mr. CASSAL asked whether the President would take steps to carry into effect the wishes of a majority at the Anniversary Meeting, that a recount of the ballot papers should be made, and the votes recorded for the two nominees for the Presidency announced to the Fellows.

Mr. VERNON HARCOURT said that, although a majority at the Anniversary Meeting had declared themselves in favour of the announcement of the numbers, it had not been found possible to make any exact announcement without going through the voting papers again, and he had hoped that, having regard to all the circumstances, it would be generally felt best to accept the result of the election as it had been recorded by the Scrutators, especially as a succinct and accurate account of what had happened at the Anniversary Meeting had been included in the minutes.

The PRESIDENT said he considered the subject closed, but promised to bring the question before the Council. He could not see that any good would result from a recount of the voting papers for the mere purpose of declaring the exact numerical majority by which the President had been elected. He hoped that long before the Council met the matter would be forgotten.

Of the following papers those marked * were read.

***50. "The hydrolysis of perthiocyanic acid." By F. D. Chattaway, M.A., and H. P. Stevens, B.A.**

When potassium thiocyanate is treated with sulphuric acid, many different substances are produced; thiocyanic acid, however, is always first liberated, and then reacts in various ways determined by the conditions of the experiment.

The best known reaction, usually represented as a simple hydrolysis of thiocyanic acid, is that by which carbon oxysulphide is commonly

prepared. Other actions, however, go on, and the carbon oxysulphide is invariably mixed with carbon dioxide, sulphur dioxide, hydrocyanic acid, and carbon bisulphide.

The authors have observed that, in addition to these, a considerable amount of thiourea is produced. This thiourea has been found to be a decomposition product of perthiocyanic acid, which is always formed in considerable quantity when acids act upon thiocyanates, and the paper deals mainly with the hydrolysis of this acid.

Perthiocyanic acid is easily hydrolysed, either by heating with water under pressure, or by heating with strong sulphuric acid, thiourea, carbon oxysulphide, and sulphur being formed. $H_2N_2C_2S_3 + H_2O = CS(NH_2)_2 + COS + S$. As the action only takes place at a comparatively high temperature, one or other of these products is invariably decomposed. When perthiocyanic acid is heated with water to about 200° in closed tubes, this action may be considered to take place first, but at the high temperature the thiourea is transformed completely into ammonium thiocyanate, while the carbon oxysulphide reacts with water, giving carbon dioxide and hydrogen sulphide so that the final action is $H_2N_2C_2S_3 + 2H_2O = NH_4NCS + CO_2 + H_2S + S$.

When perthiocyanic acid is heated with 60 per cent. sulphuric acid, a similar hydrolysis must also take place; a certain amount of the thiourea, however, escapes transformation, but the sulphur and carbon oxysulphide are oxidised by the sulphuric acid, sulphur dioxide and carbon dioxide being produced.

The thiourea found among the products of the action of strong sulphuric acid on potassium thiocyanate, is, without doubt, formed in this way by the action of the strong acid on the perthiocyanic acid first produced.

DISCUSSION.

In reply to questions from Mr. GROVES and the PRESIDENT, Mr. STEVENS stated that they had not been able to analyse the liquid supposed to be hydrogen disulphide, but they were satisfied as to its identity from a comparison of its properties with those of hydrogen disulphide specially prepared for the purpose.

***51. "The composition of cooked fish." By Katharine I. Williams.**

Twenty-two species of fresh fish and five species of preserved fish and oysters were examined after cooking.

Determinations were made of the following constituents: water; carbon and hydrogen; nitrogen (total) by Ruffle's method; nitrogen by soda lime combustion; ash; sulphur; phosphorus; fat; proteids; carbohydrates convertible into glucose; nitrates extracted by dilute alcohol; heats of combustion. The results are recorded in a series of tables.

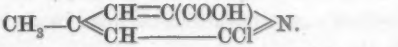
Discussion.

In reply to questions from Mr. Groves, Mr. Hehner, Mr. Sutherland, Mr. Cassal, and Professor Dunstan, Miss Williams stated that the fish, in each case, had been analysed in the condition in which it would be eaten. Details of the mode in which the fish had been prepared were given in the paper. The common opinion that fish contained much phosphorus seemed to be erroneous. Little or none of the phosphorus would be removed in cooking.

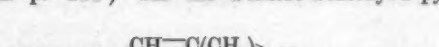
***52. "On the oxidation products of αγ-dimethyl-α′-chloropyridine." By Emily Aston, B.Sc., and J. Norman Collie, Ph.D., F.R.S.**

The present communication is an account of the continuation of some work of one of the authors with A. P. Sedgwick (Trans., 1895, 67, 399). The substance αγ-dimethyl-α′-chloropyridine was obtained by the action of phosphorus pentachloride on pseudolutidostyril. When oxidised with potassium permanganate, two isomeric acids are obtained, each having the formula $C_5H_2(CH_3)(COOH)NCl$. One (m. p. 98°) is much more soluble in water than the other and crystallises with 1 mol. of water; it produces with ferrous sulphate an orange-brown coloration. When strongly heated, it decomposes with much charring and evolution of carbon dioxide and some hydrogen chloride; the residue furnished α-chloro-γ-methylpyridine, $C_5H_3(CH_3)NCl$, b. p. 194°. Prolonged treatment with tin and hydrochloric acid gave γ-methylpicolinic acid, and this substance when distilled yielded picoline or γ-methylpyridine.

This acid (m. p. 98°) is, therefore, α-chloro-γ-methyl-α′-pyridine carboxylic acid.



The second acid obtained by the action of potassium permanganate on αγ-dimethyl-α′-chloropyridine is much less soluble in water. It melts at 214°, and on heating completely decomposes without forming chloropicoline. With ferrous sulphate, it furnished a precipitate instead of a coloration. Tin and hydrochloric acid only reduced it very slowly, and it was found to be impossible to separate the chlorine free acid from the unchanged compound. A small quantity of free α-picoline was, however, obtained by distilling the impure reduced acid, thus proving that this acid (m. p. 214°) was the α-chloro-α-methyl-α′-pyridine carboxylic acid.



Attempts were made to obtain the dicarboxylic acid from both the acids by oxidising with potassium permanganate, but without success.

ADDITIONS TO THE LIBRARY.

Donations.

Cohn, Georg. Tabellarische übersicht der Pyrazolderivate. Pp. 443. Braunschweig 1897. From the Publishers.

Bailey, G. H. First stage Inorganic Chemistry. Pp. viii + 210. London 1897. Edited by W. Briggs, M.A. From the Editor.

Dolbear, A. E. First Principles of Natural Philosophy. Pp. ix + 318. London 1897. From the Publishers.

Jones, Chapman. A Course of Elementary Experiments for Students of Practical Inorganic Chemistry. Pp. xii + 161. London 1897. From the Author.

Ricketts, P. de P., and Miller, E. H. Notes on Assaying, 1st Ed. Pp. viii + 311. New York 1897. From the Publishers.

Pamphlets.

Smith, H. G. On the Constituents of the Sap of the "Silky Oak," *Grevillea robusta*, R.Br., and the Presence of Butyric Acid therein. (Read before the Royal Society of N. S. Wales, October 7, 1896).

Smith, H. G. The dyeing properties of aromadendrin and of the tannins of *Eucalyptus kinos*. (Reprinted from the Journal of the Society of Chemical Industry.)

At the next Meeting, on Thursday, April 29th, the following papers will be received.

"Monochlordiparaconic acid and some condensations." By H. C. Myers, Ph.D.

"On the decomposition of iron pyrites." By W. A. Caldecott, B.A.

At the Meeting on Thursday, May 6th, there will be a ballot for the election of Fellows, and the following Papers will be received. The authors of those marked with an asterisk have announced their intention of being present.

* "A bunsen burner for acetylene." By A. E. Munby, M.A.

* "On the reactions between lead and the oxides of sulphur." By H. C. Jenkins and E. A. Smith.

CERTIFICATES OF CANDIDATES FOR ELECTION.

N.B.—The names of those who sign from "General Knowledge" are printed in *italics*.

The following have been proposed for election. A ballot will be held on Thursday, May 6th, 1897.

Barlow, Herbert William Leyland.
Holly Bank, Urmston, Manchester.

At present engaged in Research. M.A., M.B., Oxon. Formerly Natural Science Scholar, Trinity College, Oxford. First-class Honours in Chemistry, 1889. Junior Demonstrator, Balliol College Laboratory, 1890. Second-class Physiology, 1891. Price Scholar, London Hospital, 1894.

John Conroy. D. H. Nagel.
A. Vernon Harcourt. W. W. Fisher.
V. H. Veley.

Barlow, William,
Hillfield, Muswell Hill, N.

Fellow of the Geological and Mineralogical Societies. Has published a number of papers on geological and crystallographical subjects. Is at present engaged in studying the chemical aspects of the theory of crystalline structure.

Henry E. Armstrong. Gerald T. Moody.
F. Stanley Kipping. William J. Pope.
Sidney Williamson.

Boylan, Alfred Hunter,
"Ellerslie," Richmond Road, Ealing, W.

Analytical Chemist and Bacteriologist. Attended Professor Ramsay's course of lectures on Chemistry for 2 years at University College. With J. Parry Laws, Esq., F.I.C., 4½ years, 3 years as Articled Pupil, and subsequently as Assistant, assisting him in his investigations for the London County Council. Nine months chemist to the British Gas Light Co., Ltd., at their Norwich and Yarmouth Works, and for several months engaged by the Sulphide Corporation to assist in per-

fecting a process for the treatment of sulphide ores, assisting in the chemical and bacteriological work of the special enquiry made by the London County Council into the London Water Supply.

J. Parry Laws. W. Ramsay.
W. J. Dibdin. J. H. Coste.
Wm. Chattaway.

Brierley, James,
12, Brunswick Square, Southampton.

Public Analyst, Consulting and Analytical Chemist. Consulting Chemist to the Corporation of Southampton and Public Analyst for the Borough. Late Lecturer on Chemistry and Physics at the Hartley Institution, Southampton (23 years). Member of the Society of Public Analysts.

Percy F. Frankland. J. Lane Notter.
J. Theo. Hewitt. H. Wilson.
Otto Hehner. Bernard Dyer.

Davidge, Henry Norris,
37, Duke Street, Grosvenor Square, W.

Pharmaceutical Chemist. Member of the Pharmaceutical Society, (Major Examination).

M. Carteighe. W. Watson Will.
W. Chas. Sayers. J. L. Bullock.
Hubert E. Lindley. *James Bayne.*
Wm. Harkness.

Deverell, Louis Charles,
Onslow House, Worthing, Sussex.

Analytical Chemist. Trained in Chemistry at the Camborne School of Mines, Cornwall; for the last thirteen months (and at present) assistant to Mr. B. Kitto, F.I.C., 30 and 31, St. Swithin's Lane, E.C.

George T. Holloway. W. J. Cousins.
Cecil H. Cribb. J. J. Beringer.
W. T. Burgess. *Bernard Dyer.*

Duckham, Alexander,
Crooms Hill, Greenwich Park, S.E.

Student of Chemistry. I have studied Physics for 2, and Chemistry for 3, years at University College, London. Awarded Gold Medal for Inorganic Chemistry, and Clothworkers' Exhibition.

William Ramsay. J. Norman Collie.
A. G. Bloxam. John Shields.
Edward C. Cyril Baly. Morris W. Travers.
J. Wallace Walker. N. T. M. Wilsmore.
Alex. M. Kellas.

Fenby, Alaric Vincent Colpoys,

Hutton Grammar School, Preston.

Science Master. Junior Demonstrator in Physics, Mason College, Session 1889—90. Tutor in Chemistry, University Examination, Postal Institution, London, March—Sept., 1893. Lecturer on Chemistry, Walsall Institute, Sept.—Dec., 1893. Science Master at Hutton Grammar School, Preston, since Sept., 1894. Student of the Mason Science College, Birmingham, 1888—1892, chiefly in Chemistry and Physics. Elected an Associate of Mason College, March, 1892. B.Sc., London University, University Scholar in Chemistry, 1891; with Second Class Honours in Physics at Intermediate Science Examination, 1889.

William A. Tilden. W. W. J. Nicol.
Thomas Turner. T. Rhymer Marshall.
Harold G. Colman.

Field, Charles Henry,

The Elms, Green St. Green, Orpington, Kent.

Brewer. Studed Chemistry at the University Colleges, Nottingham and London. Also in Germany. Passed the Examination of the Institute of Chemistry.

Frank Clowes. J. Bernard Coleman.
R. Lloyd Whiteley. L. Archbutt.
J. J. Sudborough. *F. J. R. Carulla.*

Girtin, Thomas,

125A, Highbury New Park, London, N.

nt. B.A., Pembroke College, Cambridge. Chemistry Special First Class in Parts I and II. Student of Metallurgy and Assaying with Mr. F. Claudet.

W. J. Sell. S. Ruhemann.
M. M. Pattison Muir. H. J. H. Fenton.
A. Hutchinson. Arthur J. Chapman.

Guyer, R. Glode,

20, Queen's Road, St. John's Wood.

Pharmaceutical Chemist. Laboratory Chemist to Messrs. Hodgkinson, Trimber and Clarke, Manufacturing Chemists and Druggists. Studied Chemistry under Professors Attfield and Dunstan, at the Pharmaceutical Society's School, Bloomsbury; also Organic Chemistry, Practical and Theoretical, at the Finsbury Technical College, under Professor Meldola. Have been continuously engaged in Laboratory work for the past 7 years.

M. Carteighe. John Attfield.
J. H. Gladstone. Wyndham R. Dunstan.
R. Meldola. H. A. D. Jowett.

Harrie, Harold William,
298, Amhurst Road, Stoke Newington, N.

Senior Assistant in Chemical Laboratory. For 10 years engaged in the Chemical Laboratory of Messrs. Harker, Stagg and Morgan, London. From 4 to 5 years Student in the Chemical Laboratory of the City of London College. Holder of several Certificates in Inorganic and Organic Chemistry at Kensington.

Isaac S. Scarf.	Horace V. Buttfield.
E. J. Jackman.	Thos. Tyrer.
L. W. Hawkins.	*J. H. Coste.*
Bernard Dyer.	*Richard J. Moss.*

Hill, Sydney,
11, Salisbury Street, Hull.

Analytical and Technical Chemist with Blundell, Spence and Co., Limited, Hull and London, Paint, Colour, Oil, and Varnish Manufacturers. Appointed to present post in 1891. Pupil for 3 years, 1888—90, of G. Carr-Robinson, F.R.S.E., F.I.C., F.C.S., Consulting Chemist, Professor of Practical Chemistry and Lecturer at the Royal Institution Laboratory, Hull. Passed examination in Honours Practical Chemistry, also other examinations.

C. C. Graham.	G. Carr-Robinson.
M. D. Penney.	Fredk. Johnson.
Jas. Baynes.	*Allan T. Hall.*

Jones, James,
117, Old Christchurch Road, Bournemouth.

Analytical Chemist. Private Research. Desirous of keeping abreast of recent chemical discoveries.

H. Wilson.	William Fowler.
Frank H. Alcock.	Arthur P. Luff.
Chas. Umney.	*Peter MacEwan.*

W. B. Randall.

Lasseter, William James George,
10, Stanley Road, Oxford.

Science Master, Roysser School, Abingdon. Formerly Science Master, Henley Grammar School. Graduate in Honours, Nat. Science, Oxford University. Scientific Lecturer to Abingdon Town Council.

W. W. Fisher.	V. H. Veley.
John Watts.	Wm. Odling.
J. E. Marsh.	J. A. Gardner.

MacCulloch, Charles,

395, Collins Street, Melbourne, Australia.

Metallurgist. Three years in the Chemical Laboratory at Glasgow University. Employed in construction and management of Chlorination Works at Cassilis, Gippsland, treating refractory ores. At present engaged in Metallurgical research work in my private laboratory.

C. M. Aikman. Hamilton M. Wingate.
J. Holms Pollok. Thomas Gray.
Matthew A. Parker.

Mallinson, Willie Lee,

Gawthorp Green, Kirkheaton, nr. Huddersfield.

Manufacturing Chemist. Student at Huddersfield College, afterwards two and a half years assistant to Mr. George Jarmain, F.I.C., Public Analyst for the Borough of Huddersfield.

Lewis S. Cocking. Joe Frost.
James Sykes. *L. Gordon Paul.*
Hy. Ellison, Jr.

Merson, George Fowlie,

55, Northumberland Street, Newcastle-on-Tyne.

Pharmaceutical Chemist. The applicant has passed all the examinations of the Pharmaceutical Society of Great Britain, and has for several years been, and now is, Principal of the North of England School of Pharmacy, in which capacity he lectures on Chemistry and collateral Branches of Science. For several years he was Analytical Chemist on the staff of Mawson, Swan and Weddell, Newcastle-on-Tyne, Manufacturing Chemists, being Laboratory Superintendent.

M. Conroy. John Fleet.
C. Ranken. Chas. Edward Sage.
Peter MacEwan. William Duncan.
John Pattinson. *John C. Umney.*
Chas. Umney. *Wm. Martindale.*
J. Wilson Swan.

Miller, Edmund Howd,

Columbia University.

Teacher of Chemistry. Graduate of School of Mines in course of Analytical and Applied Chemistry in 1891. Master of Arts, 1892. Doctor of Philosophy, 1894. Author of "Assay of Tin," *School of Mines Quarterly*, vol. xiii, No. 4, and *Journal of Analytical and Applied Chemistry*, 1892; "Succinimid," *Journal American Chemical Society*, July, 1894; "Assay of Platinum," *School of Mines Quarterly*, vol. xvii, No. 1; "Notes on the Assay of Rich Silver Ores," *School of*

Mines Quarterly, vol. xvii, No. 2; "Notes on Ferrocyanides of Zinc and Manganese," *Journal American Chemical Society*, December, 1896; *Notes on Assaying* (with P. de P. Ricketts), Wiley and Sons, New York, 1896.

C. F. Chandler. Jas. S. C. Wells.
H. T. Vulte. *S. A. Goldschmidt.*
Arthur H. Elliott.

Mitchell, Tom,

Cemetery House, Shaw, nr. Oldham.

Analytical Chemist. For three years a Student in the evening Classes of the Chemical Dept., Owens College, 1892—95. For one year assisted in Gas Analysis in the Research Laboratory, Owens Coll., 1895–6. Has practised as an Analytical Chemist for two years.

H. B. Dixon. W. H. Perkin, Jr.
Bevan Lean. G. H. Bailey.
Wm. A. Bone.

De Morgan, Frederick Filmer,

Andely Lodge, Caeran Park, Newport (Mon.).

Student. Passed Intermediate Science, London. Studied Chemistry at the University College of South Wales and Monmouthshire, Cardiff, during the Sessions 1891—92, 1892—93, 1893—94. Passed Major Examination of the Pharmaceutical Society. Student for one year with W. Watson Will, Esq., 1895—6. Worked for four months in the laboratory of the Tharsis Copper and Sulphur Co., Cardiff (Sept., 1894—Jan., 1895). At present studying at King's College for B.Sc., London.

Claude M. Thompson. E. P. Perman.
John M. Thomson. Herbert Jackson.
Patrick H. Kirkaldy. W. Watson Will.
William H. Sodeau.

Orton, Kennedy Joseph Previte,

20, Loughborough Road, Brixton, S.W.

Hutchinson Research Student of St. John's Coll., Cambridge (in Chemistry). B.A., Cambridge. Ph.D., Heidelberg. Author of (1), with Dr. S. Ruhemann, "Studien in der Pyridin-Reibe, ein Beiträg zur Configuration der Aconitsäure," *Berlin Berichte*, 27, 3449; (2), with Dr. S. Ruhemann, "Studies in the Malonic Acid Series," *Trans. of the Chem. Society* (1895), p. 1002; (3), with Professor Auwers, "Kryoskopische Untersuchungen," *Zeitschrift. f. physikalische Chemie*, 21, 337.

William Ramsay. M. M. Pattison Muir.
Alex. M. Kellas. M. W. Travers.
N. T. M. Wilsmore. G. Nevill Huntly.
John Shields. Edward C. Cyril Baly.

Phillips, Harry Edward William,
47, Chalfont Road, Oxford.

Science Lecturer to Oxford County Council, Oxford High School, City Technical School, and Diocesan Training College. B.A. (Oxon.), Honours in Chemistry, 1895. Now engaged in research work in Chemical Laboratory, Oxford University.

Wm. Odling. W. W. Fisher.
V. H. Veley. J. E. Marsh.
John Watts. A. E. Tutton.
J. A. Gardner.

Pickard, Robert Howson,
Southfield, Priory Road, Edgbaston, Birmingham.

Student in the University at Munich. London Bachelor of Science Degree (1st Class Honours in Chemistry), "1851 Exhibition" Scholar. Joint Author with Prof. P. F. Frankland, F.R.S., of "Rotation of Optically Active Compounds in Organic Solvents" (published in Trans., 1896).

Percy F. Frankland. Charles Frederic Baker.
William A. Tilden. Walter G. Mc.Millan.
Chas. Hunt.

Tickle, Thomas,
4, Pakenham Street, London, W.C.

Salters' Research Fellow in Chemistry at the Laboratory of the Pharmaceutical Society. Work connected with a paper "The Action of Methyl Alcohol on Aconitine, by Wyndham R. Dunstan, F.R.S., Thomas Tickle, and D. H. Jackson, Ph.D.," read before the Chemical Society, June 18th, 1896. Formerly Demonstrator in Practical Chemistry in the Pharmaceutical Society's Laboratory.

J. Norman Collie. Wyndham R. Dunstan.
M. Carteighe. Harry Carter Draper.
Arthur Lapworth.

Waite, William Herbert,
Park Road, Halifax.

Science Master at Penketh School. B.A. Cantab.
W. J. Sell. S. Ruhemann.
R. Haliburton Adie. H. J. H. Fenton.
S. Skinner. M. M. Pattison Muir.

Watts, Charles Thomas Foster,
7, Cambrian Crescent, Chester.

Tutor. Science Teacher at Chester School of Science since 1893. Now responsible for Chemical Laboratory and Day Classes in Chemistry.

Science and Art Department Certificates, including First Honours in Practical Chemistry, and about 12 Advanced Certificates. London University Intermediate B.Sc., First Division.

Philip Schidrowitz. John Bairstow.
W. F. Lowe. W. B. Hards.

William Briggs.

Welsh, John,
12A, Seller Street, Chester.

Pharmaceutical Chemist. Have done a good deal of private work in the Laboratory of Chester Science School, besides having attended several full courses in Chemistry, Practical and Theoretical, Organic and Inorganic, in the above School, and also in Botany, Physics, Magnetism, and Electrical Chemistry, &c., in Liverpool School of Pharmacy. Hold Minor and Major Certificates of Pharmaceutical Society, of which Society I am a member. Hold Certificates in Advanced Stages of Inorganic Chemistry, First Practical and Second Theoretical; also First Advanced Botany in South Kensington Examinations. Have taken Honours Course, Practical Inorganic Chemistry, South Kensington Syllabus, at Chester School of Science Laboratory.

John Bairstow. Philip Schidrowitz.
W. F. Lowe. *Otto Rosenheim.*

Michael Conroy.

West, Charles Alfred,
105, Sydney Street, Chelsea, S.W.

Science Teacher. Associate of the City of London College, 1894. National Scholar for Chemistry and Physics, 1st place 1894, 1894—97. Student at the Royal College of Science under Professor Tilden. Demonstrator and Lecturer in Physics at the City of London College, 1894—97.

William A. Tilden. W. Palmer Wynne.
Chapman Jones. John A. Craw.

Isaac S. Scarf.

White, Paul Thomas,
Horton Field, West Drayton, Middlesex, and Castle Street, Saffron Hill, E.C.

Member of the firm of Alfred White and Sons, Manufacturing Chemists. Son of the late Mr. Alfred White, F.S.A., F.L.S., &c., who was also a Fellow of the Chemical Society from 1851 to his death, on March 8th, 1895.

George Matthey. David Howard.
Bernard Dyer. Rudolph Messel.
B. E. R. Newlands. Wm. Macnab.

Wm. Newlands.

RICHARD CLAY AND SONS, LIMITED, LONDON AND BUNGAY.

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PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

EDITED BY THE SECRETARIES.

No. 179. Session 1896–7.

April 29th, 1897. Professor Dewar, F.R.S., President, in the Chair.

Messrs. Arthur Croft Hill, Edward G. Guest, and Horatio Ballantyne were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Gerald Noel Brown, 8, The Esplanade, Plymouth; George Lawson Johnston, Kingswood, Sydenham Hill, S.E.; William Taverner, 1, Stapenhill Road, Burton-on-Trent.

The PRESIDENT announced that the Council had ordered a recount of the balloting papers handed in at the Anniversary Meeting. The recount would be conducted by the two Scrutators appointed by the Society at the Anniversary Meeting, in the presence of the Secretaries.

Mr. CASSAL enquired whether the actual numbers would be announced.

The PRESIDENT replied that he assumed that they would.

Of the following papers, those marked * were read:—

***53. "On the explosion of chlorine peroxide with carbonic oxide." By H. B. Dixon, M.A., F.R.S., and E. J. Russell, B.Sc.**

To test the question whether dried carbonic oxide is more readily attacked by 'nascent' than by ordinary oxygen, the authors have fired a dried mixture of chlorine peroxide and carbonic oxide. They find that the carbonic oxide is not completely burnt in the flame although the oxygen is in excess; and the drier the mixture the less carbonic oxide appears to be burnt. The results do not favour the view that 'nascent' oxygen attacks carbonic oxide more readily than ordinary oxygen.

DISCUSSION.

Dr. SCOTT thought it desirable to try the effect of some compound, such as chloride monoxide, which contained only one atom of oxygen, before concluding that 'nascent' oxygen was inoperative.

Professor ARMSTRONG referred to the difficulty of ascertaining whether a gas was completely free from water.

The PRESIDENT thought that the ultra-violet spectrum of water vapour, which he and Professor Liveing and Dr. Huggins had simultaneously discovered, would be found to be a very delicate test of its presence in flames or explosive mixtures.

Mr. CROOKES agreed with the President as to the delicacy of this test.

***54. "On the decomposition of iron pyrites." By W. A. Caldecott, B.A.**

In Watt's Dictionary (1892 edition, vol. iii, page 64) it is stated that ferrous sulphide "is formed by the reduction of Fe_2O_3 on ferric salts by decomposing organic matter in the presence of sulphates," also that "finely divided yellow pyrites (FeS_2) oxidises in air forming chiefly $FeSO_4$." T. K. Rose (*The Metallurgy of Gold*, 1896, page 343) states that "FeS_2 is oxidised by air and water, $FeSO_4$ and free H_2SO_4 being formed."

In the treatment of auriferous pyritic Witwatersrand conglomerate, a large percentage of the ore is reduced by wet crushing in the battery to an impalpable powder. This fine material constitutes "slimes," and is carried in suspension by water into extensive dams, where it settles. The slimes leaving the battery are free from ferrous sulphide, but this compound may be detected in them a few days after deposition in the dams. The settled slimes form a clayey mass, practically impermeable to air and water, and consequently subsequent oxidation of the ferrous sulphide to ferrous sulphate proceeds extremely slowly.

When iron pyrites are crushed to an impalpable powder in an iron mortar ferrous sulphide is formed.

It thus appears that ferrous sulphide and not ferrous sulphate may be the first product of the decomposition of iron pyrites.

Owing to the almost total absence of acidity in slimes deposited as above, even when containing 0·89 per cent. ferrous sulphide, it is probable that under these conditions FeS_2 undergoes dissociation, and the sulphur is separated as such; the author is engaged in further investigating this subject.

***55. "Monochlordiparaconic acid and some condensations." By Henry C. Myers, Ph.D.**

An attempt to prepare methylparaconic acid by the reduction of the trichlor-acid furnished the dichlor-acid, which on treatment with

barium-hydroxide suffered condensation, forming the acid $C_9H_9ClO_2$, which has been called monochlordiparaconic acid; its constitution is under investigation. This acid loses its chlorine on treatment with nascent hydrogen, producing a compound having in all probability the formula $C_9H_{12}O_2$, but it is so unstable that its investigation is very difficult. These condensations are being further investigated.

56. "Corydaline. Part V." By James J. Dobbie, M.A., D.Sc., and Fred Marsden, M.Sc., Ph.D.

When corydaline is heated on the water bath with very dilute nitric acid (about 1 : 20), a difficultly soluble nitrate, $C_{22}H_{29}NO_4 \cdot HNO_3$, is first formed.

On further heating, the solution becomes dark red in colour, and soon ceases to give any precipitate on testing with ammonia. If at this stage the solution be allowed to cool, groups of bright yellow prismatic crystals separate out on the sides of the vessel. The crystals consist of the nitrate of a base—dehydrocorydaline—differing from corydaline by four atoms of hydrogen (*cf.* Trans., 1897, **72**, i, 175). The free base is very soluble in water and alcohol, and is difficult to obtain in crystals. The nitrate, $C_{22}H_{25}NO_4 \cdot HNO_3$, the chloride $C_{22}H_{25}NO_4 \cdot HCl$, the platinochloride $(C_{22}H_{25}NO_4 \cdot HCl)_2PtCl_4$, and the chloroform compound, $C_{22}H_{25}NO_4 \cdot CHCl_3$, are described. The solutions of dehydrocorydaline and its salts have an intense yellow colour, and give a vivid green colour with blue litmus. Reducing agents reconvert dehydrocorydaline into optically inactive corydaline.

If concentration of the acid solution be continued beyond the point at which dehydrocorydaline is formed until platinum chloride no longer gives a precipitate, yellow coloured crystals of an acid melting at 218° separate out on cooling. This acid, to which, for convenience of reference, the name *corydic* is temporarily given, is readily soluble in hot water and in alcohol, but insoluble in ether. Its aqueous solution has an intense yellow colour, and does not give precipitates with any of the metals in aqueous solution.

A silver salt, $C_{18}H_{15}NO_6Ag_2$, is obtained by precipitating an alcoholic solution of the potassium salt of the acid with an alcoholic solution of silver nitrate. Corydic acid contains two methoxy-groups and is dibasic. Its formula is $C_{14}H_9N(OCH_3)_2(COOH_2),\frac{1}{2}H_2O$. When heated with hydrogen iodide, it yields a highly insoluble phenolic acid, $C_{14}H_9N(OH)_2(CO \cdot OH)_2 \cdot 2H_2O$, which separates from a large quantity of hot water in brilliant yellow spangles. The lead salt of this derivative, dried at 130°, has the composition $C_{16}H_{11}NO_6 \cdot Pb$.

When corydic acid is boiled with a solution of potassium permanganate, it yields a mixture of at least four acids.

(1) An acid, $C_{12}H_6N(OCH_3)_2(CO_2H)_3$, which crystallises from hot water in small, white, acicular crystals melting at 228°. This acid, which is the chief product of the oxidation, contains two methoxy-groups. A silver salt having the composition $C_{17}H_{12}NO_8Ag_3$ has been prepared. (2) A hemipinic acid, yielding an ethylimide which melts at 228°, and differs therefore from the hemipinic acid previously described as occurring amongst the products of oxidation of corydaline with potassium permanganate. It is thus established that corydaline contains two benzene nuclei, and the formation of corydic acid from the alkaloid is easily explained on the assumption that one of the rings is oxidised. (3) A nitrogenous acid melting at 208° which contains no methoxy-groups and gives a faint brownish-yellow colour with ferrous sulphate solution, and evolves a strong odour of pyridine when heated with lime. This acid has the formula $C_9H_7NO_6 \cdot H_2O$, and is apparently a methylpyridine tricarboxylic acid. It is not identical with any of the known acids of this composition. It forms a silver salt, $C_9H_4NO_6Ag_3$, and gives precipitates with lead, barium, and copper. (4) A nitrogenous acid melting at 243°, which gives a yellowish-red colour with ferrous sulphate and contains methoxyl.

Oxalic acid and the nitrogenous acid melting at 208° were obtained from the mother liquors of corydic acid.

May 6th, 1897. Professor Dewar, F.R.S., President, in the Chair.

Certificates were read for the first time in favour of Messrs. William Ackroyd, 9, Grandsmere Place, Halifax; William Malam Brothers, Beechwood House, Prestwich, near Manchester; William Cranfield, 5, Second Avenue, Halifax; A. F. Bilderbeck Gomez, 24A, Alfred Place West, South Kensington; Frederick Roscoe Grundy, B.Sc., 20, Derby Road, Douglas, Isle of Man; Edward Halliwell, Alexandra Crescent, Dewsbury; Harold Harman, Brewers Sugar Co., Greenock; William Robertson Pollock, Kirkland, Bonhill, Dumbarton.

The PRESIDENT stated that, in accordance with the instructions of the Council, the two Scrutators, in the presence of the Secretaries, had recounted the votes recorded for the Presidency at the Anniversary Meeting. The Scrutators' report would be presented to the Council in due course, but he thought he might now venture to say that he learned from the Senior Secretary that the votes accepted by the Scrutators were 166 for the Council's nominee, and 152 against.

The following were duly elected Fellows of the Society. Messrs. Herbert W. L. Barlow, M.A., M.B.; William Barlow; Alfred Hunter Boylan; James Brierley; Henry Norris Davidge; Louis Charles Deverell; Alexander Duckham; Alaric Vincent C. Fenby, B.Sc.; Charles Henry Field; Thomas Girtin, B.A.; R. Glode Guyer; Harold

William Harrie; Sydney Hill; W. J. G. Lasseter, M.A.; Charles Macculloch; Willie Lee Mallinson; George Fowlie Merson; Edmund Howd Miller, M.A., Ph.D.; Tom Mitchell; Frederick Filmer de Morgan; Joseph Previte K. Orton, B.A., Ph.D.; Harry E. W. Phillips, B.A.; Robert Howson Pickard, B.Sc.; Thomas Tickle; William Herbert Waite, B.A.; Charles Thomas Foster Watts; John Welsh; Charles Alfred West; Paul Thomas White.

Of the following papers, those marked * were read.

***57. "A Bunsen burner for acetylene." By A. E. Munby, M.A.**

The cheap production of calcium carbide has placed a powerful illuminant within the reach of those who possess no gas supply, but so far little has been heard of the use of acetylene as a heating agent. Our laboratory is, as far as we know, the first to make use of the gas for this purpose. We employ a bunsen burner of special dimensions, the tube being five milimetres in internal diameter. A slightly wider tube may be used, provided the mouth be curved inwards, so that the actual exit does not exceed the diameter mentioned; if larger, the flame tends to strike down. The gas jet is very small, being only capable of delivering about one cubic foot of acetylene per hour under six inches water pressure, such a rate of consumption giving an ordinary working flame. The air holes and collar are arranged as in an ordinary bunsen, the exact size of the former not being of much importance provided they be large enough to admit the air required. The burner is protected with a cap, when not in use, as its efficiency depends upon the jet maintaining its dimemsions. A generator capable of giving gas under seven inches water pressure with the full number of burners in use is required. Under this pressure a large, perfectly blue flame is obtained, which may be turned down to what may be termed a quarter bunsen flame, equivalent to burning the gas under three to four inches water pressure. This is the smallest pressure with which the burner will give a non-luminous flame; when turned lower, the zone of partial combustion appears, since the draught is then insufficient.

The heating effect of the flame is of course very great, enabling one to dispense with the blow-pipe for some operations, such as small fusions. From a few experiments on heating equal quantities of water under like conditions with coal gas and acetylene, it would seem that in practice, for equal volumes burnt, the latter has nearly twice the heating power of the former.

The use of the gas should do much to stimulate research in country places and on private estates.

***58. "The reactions between lead and the oxides of sulphur." By Henry C. Jenkins and Ernest A. Smith.**

The authors draw attention to the fact mentioned by one of them during the discussion on Mr. Hannay's paper (Proc., 1894, 10, 113, 151,) that when lead is heated to high temperatures and a current of sulphur dioxide passed through it, lead sulphide and oxide are formed. They have conducted experiments with a view to see whether the observations accounted for the anomalies hitherto met with whenever a full explanation of the chemistry of lead smelting in the reverberatory furnace has been attempted. Mr. Hannay had sought to explain these anomalies by the assumption that a volatile compound, PbS_2O_2, was formed, basing his evidence on an observation that in some experiments of his where air was passed over heated galena, he only obtained one-half of the lead in the metallic state. He gave the equation $2PbS + O_2 = Pb + PbS_2O_2$ as representing what occurred. The experiments have been carefully repeated by the authors, who find that the ratio of lead obtained to lead volatilised is not constant but varies, and is entirely dependent on the velocity of the current of air, indicating that no such reaction exists and that the ratio found in Mr. Hannay's experiments was the result of the accidental coincidence of his experimental conditions.

The authors, on continuing the experiments, found on heating lead sulphide and lead sulphate in a vacuum, that a reaction having sulphur dioxide as a product occurred, and they found that the amount of residual lead sulphide and oxide was dependent on the duration as well as on the temperature of the experiment. They then proceeded to separately test the pairs of bodies supposed to be present, with a view to discover if secondary or reversed reaction occurred. On heating lead and lead sulphate, they always obtained lead sulphide in the product in amounts varying with the duration of the experiment and the length of time that it occupied.

On heating lead and sulphur dioxide together, they found that at moderately elevated temperatures lead sulphide and sulphuric anhydride are formed in each other's presence, and that this leads to the formation, first of lead oxide and then of lead sulphate, the action being represented more or less completely by the equations $Pb + 3SO_2 = PbS + 2SO_3$, $Pb + 2SO_3 = PbSO_4 + SO_2$, or more simply, $2Pb + 2SO_2 = PbS + PbSO_4$, the main determining condition as to the relative amount of the products being that of the temperature at which the experiment is performed. One of the authors is continuing the investigation of the exact condition of the equilibrium.

The last of these equations occurring in the presence of excess of

sulphur dioxide, is the exact inverse of the main ones of the metallurgy of lead as stated by Dr. Percy, and requires a supply of air by which to sweep away the sulphur dioxide as soon as it is liberated. The authors submit that, as the new equations quite account for the anomalies to which attention has been drawn, there is now no reason whatever to doubt that the equations given by Dr. Percy, $Pb + PbSO_4 = 2PbO + SO_2$, $PbS + PbSO_4 = 2Pb + 2SO_2$, as well as $PbS + 2PbO = 3Pb + SO_2$, represent the facts and form the basis of the metallurgy of lead.

Discussion.

Professor Roberts-Austen said that he was much gratified by the fact that the accuracy of the time-honoured equations given by his distinguished predecessor, Dr. Percy, as representing the metallurgy of lead, had been abundantly justified by work done in the Metallurgical Laboratory of the Royal College of Science. He could testify to the extreme care which Messrs. Jenkins and Smith had given to the work, and the reversible reactions they had discovered were not only very interesting, but of much industrial importance. In justice to Mr. Hannay, it might be conceded that the singular nature of the reactions discovered by the authors of the paper justified Mr. Hannay in questioning the accuracy of the old equations, and it was satisfactory that the difficulty had now been solved.

The President, Mr. Groves, and Professor Armstrong thought the author's experiments showed that it was unnecessary to suppose that any new compound of lead and sulphur was concerned in the metallurgical process.

***59. "X Ray photographs of solid alloys." By C. T. Heycock, F.R.S., and F. H. Neville.**

In a previous communication (Trans., 1889, **55**, 666), we discussed the behaviour of gold in sodium and the state of the gold in the solid alloy. We have lately examined alloys of gold and sodium by cutting thin sections from cylinders of the alloy of various concentrations, placing these on a photographic plate, and photographing them by means of the X rays.

On account of the much greater transparency of sodium to these rays as compared with gold, the individual crystals of the alloy are clearly shown. The plates were about 12 mm. thick, and the alloy had been allowed to cool and solidify very slowly. Pure sodium shows no crystalline structure, but an alloy containing 3 per cent. of gold shows a mass of transparent sodium crystals, with dark spaces between the crystals where the gold has concentrated during the process of solidification.

A 10 per cent. alloy of gold shows the same phenomena, but the crystals of sodium are narrower, and the dark spaces occupy a larger area.

The appearance of the sodium crystals strongly recalls the fern-like pattern seen when ammonia chloride is crystallised on a microscopic plate, doubtless due to the fact that sodium, like so many other metals, crystallises in the regular system. An eutectic alloy of gold and sodium (23·1 per cent. gold) shows, as one would expect, scarcely any structure, because the crystals of gold and sodium separate out simultaneously, and are too minute to be detected by such a method.

A solution obtained by saturating sodium with gold at a temperature considerably above the melting point of sodium shows a net-work of black, opaque needles, which are no doubt crystals of gold which have separated and grown to a considerable size as the liquid cooled.

No sodium crystals are here visible, as the groundwork consisted of the eutectic alloy. We have been able to demonstrate the internal structure of a solid alloy, and to show that the process of solidification is strictly comparable to that of a saline solution, the details being perfectly visible to the naked eye.

We have already examined some aluminium alloys by this method, and hope to present a complete account of the work to the Society. The method will probably be applicable in all cases where there is a considerable difference in transparency between the metals of an alloy.

Discussion.

Professor Roberts-Austen said that the use of Röntgen rays for revealing the structure of certain alloys possessed advantages when it was desirable to view the alloys as transparent, as distinguished from the structure shown by a section in a single plane. The structure of alloys as revealed by microphotography had now attained great perfection, notably in the hands of M. Osmond in France, and it was a subject to which Professor Austen had recently given much attention; but the X rays might be very useful in the case of alloys containing one transparent metal. When Röntgen's great discovery was first published, Professor Austen had examined the relative transparency of certain metals, and endeavoured to detect the difference between hard and soft steel, but the sections of steel employed were too thick, and the experiments were abandoned.

It had been shown by Osmond and by Charpy that eutectic alloys have a pearly structure, and Professor Austen thought that the gold-sodium eutectic shown on the screen by Mr. Heycock also had the pearly structure. As a good example of the distribution produced by freezing, Professor Austen stated that if a triple alloy of copper, antimony, and

lead was cast as a rod and fractured transversely, a purple ring of the "regulus of Venus" (the copper antimony alloy) surrounded the grey alloyed lead which was driven to the centre, so that there was a grey rod inside a purple tube. He hoped that Messrs. Heycock and Neville, who were so greatly extending our knowledge of alloys, would continue their investigations.

The PRESIDENT remarked that this was an important and interesting communication, as illustrating the service the Röntgen rays might be to the chemist. Soon after the announcement of the original discovery, he made experiments on the transparency of the elements to the new rays, and took a number of photographs. In a verbal communication to the Royal Society, he had announced that the opacity of elements to the rays increased in the same series with their atomic weight. He thought the rays might sometimes be of use in settling doubtful cases of atomic weight. For example, if liquid or solid argon were found to be less transparent than oxygen or nitrogen in a similar condition, it might be safely concluded that its atomic weight is higher than that of either of the other constituents of air.

RESEARCH FUND.

A meeting of the Research Fund Committee will be held in June. Applications for grants, accompanied by full particulars, should be sent to the Secretaries before June 8th.

LIST OF FELLOWS.

A new list of Officers and Fellows of the Chemical Society being in course of preparation, it is requested that Fellows will send any alteration of address, without delay, to the Assistant Secretary, Burlington House, London, W.

At the next meeting, on Thursday, May 20th, the following Papers will be received. The authors of those marked with an asterisk have announced their intention of being present.

* "The theory of osmotic pressure and the hypothesis of electrolytic dissociation." By Holland Crompton.

* "Molecular rotations of optically active salts." By Holland Crompton.

* "Heats of neutralisation of acids and bases in dilute aqueous solution." By Holland Crompton.

* "A comparative crystallographical study of the normal selenates of potassium, rubidium, and cæsium." By A. E. Tutton.

* "The platinum-silver alloys; their solubility in nitric acid." By John Spiller.

RICHARD CLAY AND SONS, LIMITED, LONDON AND BUNGAY.

Issued 1/6/1897.

PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

EDITED BY THE SECRETARIES.

No. 180. Session 1896–7.

May 20th, 1897. Professor Dewar, F.R.S., President, in the Chair.

Messrs. H. E. Gardner, William Barlow and Paul Thomas White were formally admitted Fellows of this Society.

Certificates were read for the first time in favour of Messrs. Walter Harry Barlow, 152, Osbaldiston Road, Stoke Newington, N.; Ernest Stuart Cameron, 51, Pembroke Road, Dublin; Medwin Caspar Clutterbuck, B.Sc., Ph.D., 61, Beaconsfield Villas, Brighton; Frank William Harbord, Egham; B. J. Harrington, Ph.D., McGill College, Montreal; A. G. Kidston Hunter, Princes Street, Dunedin, N.Z.; John Edwin Mackenzie, B.Sc., Ph.D., 7, Ramsay Garden, Edinburgh; Lionel Walter Kennedy Scargill, B.A., 14, Brunswick Place, W. Brighton; James Porter Shenton, 34, Lansdowne Road, W. Didsbury, Manchester.

Of the following papers, those marked * were read:—

***60. "The theory of osmotic pressure and the hypothesis of electrolytic dissociation." By Holland Crompton.**

The author applies the results obtained by Guye, Ramsay and Shields, and others in their investigations on the molecular complexity of liquids to the theory of osmotic pressure. It is found that Van't Hoff's view, that the osmotic pressure of the dissolved substance is in dilute solution equal to the pressure which the substance would exercise in the same volume if in the gaseous state, is applicable when both the dissolved substance and the solvent form normal or monomolecular liquids. It may also apply if both liquids are associated. But if the

dissolved substance is associated and the solvent is monomolecular, the osmotic pressure is then smaller than the theoretical, and becomes inversely proportional to the factor of association x_1 of the dissolved substance. If the solvent is associated and the dissolved compound is monomolecular, the osmotic pressure is greater than the theoretical, and is directly proportional to the factor of association x of the solvent. If the solvent has also an abnormal vapour density, the factor of association of the vapour being a, the osmotic pressure is directly proportional to x/a.

By application of the above conclusions, it is shown that the latent heat of fusion r, melting point on the absolute scale T, and density at the melting point, d, of a liquid are connected by the expression $rd/T = \text{const.}$ in the case of monomolecular liquids, or $rdx/Ta = \text{const.}$ in the case of associated liquids. The mean value of the constant is 0·099, or roughly 0·1. This formula is exactly similar to the Trouton formula, which connects the latent heat of vaporisation, gaseous density, and boiling point on the absolute scale of liquids.

The molecular reduction of the freezing point for monomolecular substances in monomolecular solvents is given by Van't Hoff's formula, $E = 0{\cdot}01976\ T^2/r$, or by the derived formula $E = 0{\cdot}2\ Td$. If, however, the dissolved substance or the solvent are associated, this formula no longer applies, but $E = 0{\cdot}01976\ T^2x/rax_1$, or $E = 0{\cdot}2Td/x_1$. Exceptions to Van't Hoff's formula for the molecular reduction of the freezing point appear, therefore, whenever association of either the dissolved substance or the solvent takes place, and it is shown that those exceptions observed in the case of electrolytes in aqueous solution are in perfect keeping with the view that electrolytes are monomolecular compounds in solution in an associated solvent, *e.g.*, water. The hypothesis of electrolytic dissociation is not only unnecessary in explanation of these exceptions, but is inconsistent with what is now known of the molecular character of liquids.

A connection is supposed to exist between the specific inductive capacity of a liquid and its power of promoting electrolytic dissociation. The author shows that it is only associated liquids that have high specific inductive capacities, and that the specific inductive capacity is approximately proportional to the cube of the factor of association of a liquid. It is therefore not on the degree of electrolytic dissociation of the dissolved substance, but on the degree of association of the solvent, that the conductivity depends, and the view is taken that electrolytes are salts in the monomolecular fluid state in solution in associated solvents.

***61. "Molecular rotations of optically active salts." By Holland Crompton.**

A fact which is usually quoted as strong evidence in favour of the hypothesis of electrolytic dissociation, is that salts which contain a common optically active ion—either positive or negative—exhibit, in sufficiently dilute aqueous solution, the same equivalent rotatory power. If, however, electrolytes are salts in the monomolecular fluid condition (preceding paper), the observed regularities indicate that monomolecular salts which contain a common optically active radicle have the same equivalent rotation. Those peculiarities which have been observed in the case of the equivalent rotations of optically active electrolytes in aqueous solution, are shown by the author to be also exhibited by the amylic salts of certain organic acids, when these are examined in the free state and not in solution in any solvent. As electrolytic dissociation is in this case entirely out of the question, the hypothesis becomes an unnecessary one in other instances, and the behaviour of optically active electrolytes is merely in keeping with that of other optically active monomolecular salts.

***62. "Heats of neutralisation of acids and bases in dilute aqueous solution." By Holland Crompton.**

The constancy of the heat of neutralisation of an acid by a base is usually explained in accordance with the electrolytic dissociation hypothesis by the assumption that the acid, base, and the resulting salt are all in a dissociated state, and that the only change occurring in the system is the formation of water from its ions. In this paper, the author calls attention to the fact that from Thomsen's *Thermochemische Untersuchungen, Band IV.*, it may be inferred that the replacement in any monomolecular organic compound RH of the H atom by one and the same radicle M, is attended with a constant heat change, which is independent of the character of R, and that for monomolecular compounds the heat of the reaction RH − H + M is constant if M is constant and independent of variations in R. From this it also follows that the heat of the reaction ROH − OH + M is constant. In the neutralisation of an acid RH by a base MOH, we have the changes M − OH, R − H, M + R, H + OH. If M is kept constant then two terms in the reaction will be constant, M − OH and H + OH. The only variation is then in R − H and M + R. But as shown above, for monomolecular compounds RH − H + M is attended with a heat change that is independent of R, and hence if acids and bases in dilute aqueous solution are monomolecular compounds, the heat of neutralisation of any acid by one and the same base is a constant quantity. It may be shown in similar

manner that the heat of neutralisation of any base by one and the same acid is constant, and hence the heats of neutralisation of acids by bases are always the same. The hypothesis of electrolytic dissociation is unnecessary in explanation of the observed phenomena, if it be granted that the dissolved electrolytes are monomolecular compounds.

In the above, since OH is simply another negative radicle R, the heat of the reactions M – OH and H + OH might be expected to exactly balance that of the reactions H – R and M + R. This is probably the case when the reactions do not occur in dilute aqueous solution. But in solution while the acid, base, and salt are in a condition comparable with that of their vapours, the water which is formed in the reaction must be transformed from that state to the liquid state of the solvent by which it is surrounded. This implies that the heat of neutralisation of an equivalent of an acid by an equivalent of a base in aqueous solution contains as main factor the heat of condensation of a molecule of water. This latter quality has a value of about 10,800 cal., and the mean value of the heat of neutralisation is 13,500 cal. The difference between the two values is to be mainly attributed to the state of partial association of the base.

Discussion.

Mr. Pickering said whether Mr. Crompton had established his views or not, he had succeeded in throwing much new light on the subject under examination, and had given us further evidence that the theory of dissociation was not the only one through which we might look for an explanation of the phenomena of dissolution.

By way of criticism, the speaker suggested that the means of recognising a liquid to be of the associated or non-associated class at the freezing temperatures was somewhat imperfect, and might, in many cases, lead to erroneous conclusions. He doubted, also, whether the numbers obtained showed that the same solvent indicated consistently the same degree of association when pitted against various monomolecular solutes, as should be the case, and whether the same associated solute, when pitted against various monomolecular solvents, gave similarly consistent results. A stronger objection, however, might be raised in the behaviour of diatomic and triatomic electrolytes in water. According to Mr. Crompton's views, these should both give values of 55·2 for the depression of the freezing point when in extreme dilution; the triatomic electrolytes do so, but diatomic electrolytes give values which show little or no tendency to surpass 37, which is only double instead of three times the 'normal' value.

As regards the heat of neutralisation, the speaker considered Mr.

Crompton's application of a general principle which has been established in organic transformations to similar transformations in inorganic solutions to be both legitimate and ingenious. The simplicity of the principle for organic substances, no doubt, depends on the fact that these substances are nearly saturated compounds, and in dilute solutions of inorganic compounds we are probably also dealing with saturated compounds. Some years ago, the speaker brought before the Society an explanation of the constancy of the heat of neutralisation which was based on chemical grounds, without recourse to the theory of dissociation. Residual affinity was the explanation which was offered, and Mr. Crompton's explanation could be improved by taking residual affinity into consideration. Mr. Crompton accounts for the heat evolved on neutralisation by the condensation of the molecule of water formed; this condensation should certainly be recognised (a fact which the speaker had overlooked in his own communication on the subject), but the heat evolved by it falls short of that of neutralisation by some 3000 cal., and it seems probable that this excess may be accounted for by the salt formed becoming, in the presence of water, more fully saturated than either the acid or the alkali. Each of these latter contains a radicle, H and OH, which is identical with one of the radicles in water itself, and such compounds would, therefore, probably not have their residual affinity entirely saturated by the water, whereas this is not so with the salt, and there is nothing in its case to prevent complete saturation.

Mr. W. C. D. Whetham said that although it was impossible to criticise such an interesting paper without having considered its details, he would like to ask Mr. Crompton how he would explain the phenomena of electrical conductivity. On the theory that the ions were free from each other, the observed fact that the conductivity of a dilute solution varied as the concentration was at once explained. The alternative supposition, that the ions worked their way through the solution by means of a continual series of interchanges between the opposite parts of molecules at the instants of collision, would lead to a different result, for the frequency with which such collisions would occur, and therefore the ionic velocities, must vary as the square of the concentration, and since the conductivity depended on the product of the number of ions and their average velocity, it would be proportional to the cube of the concentration.

Then, again, the fact that the velocity of an ion in dilute solution was independent of the other ion present, not only as calculated from the conductivity, but also as directly observed, seemed to favour the idea of dissociation, and was of greater weight than other additive relations, since it involved the properties of the ions when in motion.

The successful calculation of potential differences at the contact of

two solutions on the assumption that the faster-travelling ion moved independently of the other, and so diffused more quickly, must also be remembered. Such phenomena as these must be explained before the dissociation theory could be abandoned. No doubt the theory presented many difficulties, and a successful attempt to explain the facts in some other way would be of extreme interest; but at present the evidence in favour of the dissociation theory seemed very strong.

Dr. SHIELDS, after referring to the difficulty of discussing the paper until all the details were before them, stated that he was not satisfied that Mr. Crompton had made out his case that abnormally large osmotic pressures were due to the association of the solvent. According to the well-known equation, the osmotic pressure, π, of a solution containing n molecules of dissolved substance in N molecules of solvent is represented thus:

$$\pi = \frac{n}{N} \cdot \frac{RT1000\rho}{M}$$

where M denotes the molecular weight of the solvent, ρ the specific gravity of the solution, T the absolute temperature, and R is a constant, viz., 0·0819 litre-atmospheres, when we express the osmotic pressure in atmospheres and the volume of the solution containing 1 g-molecule in litres. In the above equation, the product NM is the weight in grams of the solution containing n g-mols. of the dissolved substances.

If we make up a dilute solution to contain, by intention, n g-mols. of dissolved substance in N g-mols. of a solvent supposed, in the first instance, to be normal or monomolecular, then we get a certain definite value for the osmotic pressure. If, however, the solvent is associated, and x is a measure of its molecular complexity, then instead of having weighed out N g-mols. of solvent, we have in reality only N/x, and since the weight of the solution remains the same, the osmotic pressure must be

$$\pi = \frac{n}{N/x} \cdot \frac{RT1000\rho}{xM}$$

or in other words remain uninfluenced by the degree of association of the solvent.

As regards aqueous salt solutions, Dr. Shields thought Mr. Crompton would encounter serious difficulties in attempting to explain why dilute solutions of binary compounds, such as potassium chloride, had a maximum osmotic pressure of twice the theoretical value, whilst compounds like calcium chloride gave three times the pressure one would expect.

Dr. Shields also called attention to the fact that associated liquids such as water become less associated as the temperature is raised, and asked whether when the particular temperature were reached at which

water becomes 'normal,' salt solutions also become 'normal,' *i.e.*, show the theoretical osmotic pressure corresponding to that temperature and otherwise behave like indifferent substances or non-electrolytes.

Mr. CROMPTON, in reply, explained that in assigning to a particular liquid a monomolecular or an associated character the general results of the work of Guye, Ramsay and Shields and others had as far as possible been adhered to. That the molecular reduction of the freezing point of water by electrolytes was in certain cases, even in the most dilute solutions, below the value required for monomolecular compounds, indicated that the salt was originally associated and that the complex molecules only broke down slowly with rising dilution. Similar instances could be observed in the case of solutions of associated compounds in other solvents, *e.g.*, benzene. Alcohol, which in concentrated solution in benzene gave a molecular weight far higher than the normal, would be found to give correct values in very dilute solution. On the other hand, acetic acid gave even in very dilute solution in benzene a molecular weight of about 110 in place of 60, the splitting up of the associated molecules taking place apparently with greater difficulty in the case of this compound than in that of alcohol. The adequacy of the dissociation hypothesis to explain the electrical properties of salt solutions had not been called in question, but it had been shown that the hypothesis gave no true account of certain other properties of salt solutions which it had hitherto professed to explain. The additive character of the molecular conductivities of dilute salt solutions was merely in keeping with the additive character of nearly all the properties of monomolecular compounds in the fluid condition, as, for example, the molecular volumes, the molecular refractions, the molecular viscosities. If a dissociation hypothesis were adopted to explain additive properties in one case, this would have to be extended to all, and such a thing as a monomolecular fluid compound would be non-existent.

***63. "A comparative crystallographical study of the normal selenates of potassium, rubidium, and cæsium." By A. E. Tutton.**

The main conclusions of this investigation, which is analogous to the one formerly presented concerning the corresponding sulphates (Trans, 1894, **65**, 628), are as follows.

1. The order of solubility of the three salts follows that of the atomic weights of the three respective metals contained.

2. The values of the morphological angles of the crystals of rubidium selenate are without exception intermediate between those of the analogous angles of the potassium and cæsium salts. The angles are therefore a function of the atomic weight of the metal present.

3. The morphological axial ratios of rubidium selenate are likewise intermediate.

4. The usual habits of the crystals of the three salts exhibit a progressive development of the primary forms, following the progressive change in atomic weight.

5. The directions of cleavage are identical.

6. The relative density and molecular volume increase when a lighter is replaced by a heavier alkali metal. The increase in density is greater when potassium is replaced by rubidium than when the latter is replaced by cæsium, and the increase in molecular volume is, on the contrary, greater when rubidium is replaced by cæsium. The replacement of sulphur in the sulphates by selenium is accompanied by an increase of molecular volume varying from 6·5 to 6·7 inversely as the weight of the initial molecule.

7. The replacement of potassium by rubidium, and of the latter by cæsium, is accompanied in each case by an increase in the separation of the centres of contiguous units of the homogeneous crystal structure, along the directions of each of the morphological axes, the influence of the nature of the alkali metal becoming relatively greater as the atomic weight rises. An extension of volume in all directions also accompanies the replacement of sulphur by selenium.

8. An increase of refractive index is observed to accompany an increase in the atomic weight of the alkali metal, and the increase becomes relatively greater as the atomic weight rises. The replacement of sulphur by selenium is also accompanied by an increase of refractive index, and such increase diminishes in amount as the weight of the initial molecule increases.

9. If the closed optical ellipsoidal figures, the optical indicatrices, of the three salts were constructed about the same origin, the indicatrix of the cæsium salt would contain within it that of the rubidium salt, and this again would contain that of the potassium salt. The indicatrix of the rubidium salt would lie nearer to that corresponding to the potassium salt.

10. The replacement of one alkali metal by another of higher atomic weight is accompanied by a diminution of the already feeble double refraction. In the convergence of the axial values of the optical indicatrix towards unity the c value proceeds much more rapidly than the others.

11. The latter fact causes a reversion of the sign of double refraction from positive to negative on attaining the cæsium salt.

12. The optic axial angles are precisely such as would naturally follow from the progressive development of the optical indicatrix; a change of direction of the acute bisectrix and of the optic axial plane occurs

when the cæsium salt is reached, as the direct result of the continuity of the progression according to atomic weight.

13. The optical properties of the selenates exhibit marked specific differences from those of the sulphates, owing to the progressively different effect of replacing sulphur by selenium in the three sulphates, but the whole of the relationships of these optical properties exhibited by the three salts of each group are of a precisely parallel nature, being functions in each case of the atomic weight of the alkali metal which they contain.

14. Progressive changes occur in the optical properties on raising the temperature, following, even to the least detail, the order of the atomic weights. An interesting direct consequence is that a 60° prism of cæsium selenate whose vibration-directions are parallel to *b* and *c* affords at 90° C. only one image of the spectrometer slit, the two images usually observed coinciding at this temperature, the crystal being then apparently uniaxial.

15. A further consequence of the foregoing is that the crystals of cæsium selenate exhibit unique interference phenomena in convergent polarised light when their temperature is raised, including crossed axial plane dispersion, and two reversals of the sign of double refraction. Section-plates perpendicular to all three axes in turn require to be employed in order to follow the optic axial changes even as far as 280° C.

16. The whole of the molecular optical constants of rubidium selenate are intermediate between those of potassium and cæsium selenates. The replacement of sulphur by selenium is acompanied by an increase of molecular refraction of 3·4—3·8 Lorenz or 6·2—6·7 Gladstone units, according to the direction chosen for comparison. The relations of the three salts of each group as regards molecular refraction are identical, but the actual differences are slightly greater in the selenate group than in the sulphate group.

17. The molecular refraction of each of the three selenates for the state of solution in water is approximately the same as the mean of the three values for the crystal. When potassium selenate is dissolved in water, its refraction equivalent rises by 2·8 per cent; in the case of rubidium sulphate, a less rise of 1·0 per cent. is observed, while for cæsium selenate there is no longer a rise but a decrease, to the extent of 0·5 per cent. These slight differences, due to change of state, thus exhibit a progression varying directly as the specific refractive energy and inversely as the atomic weight of the alkali metal contained in the salt. After subjecting Kanonnikoff's value for dissolved potassium sulphate to revision, precisely similar differences for the two states are shown to exist in the sulphate group.

18. The author finally concludes as regards the selenates that—

The whole of the morphological and physical properties of the crystals

of the rhombic normal selenates of potassium, rubidium, and cæsium are functions of the atomic weight of the alkali metal present.

19. It is shown that the joint results of the investigations of the sulphates and selenates agree with the assumption that—

The characters of the crystals of isomorphous series are functions of the atomic weight of the interchangeable elements, belonging to the same family group, which give rise to the series.

DISCUSSION.

Dr. GLADSTONE remarked that everyone recognised in a general way that in groups of analogous elements there is a gradual progression in the properties, the middle member of the group being intermediate, not only in atomic weight, but also in other respects. The value of Mr. Tutton's elaborate papers, is, that he has proved this up to the hilt quantitatively in the case of two similar, well defined groups of salts, and that with regard to a large number of properties. The change in the specific refraction of the selenates of the alkalis in their crystalline and their dissolved condition is especially instructive, as it involves the change from *plus* in potassium and rubidium to *minus* in cæsium. The correction of Kanonnikoff's number for the potassium sulphate which Mr. Tutton has made brings the atomic refraction back to a figure practically identical with that published in Dr. Gladstone's paper of 1870, viz., 33·11.

***64. "The platinum-silver alloys; their solubility in nitric acid." By John Spiller.**

Referring to the published statements in the text-books, and particularly to those in Percy's *Metallurgy* and Bloxam's *Chemistry*, according to which 5 or even 9 per cent. of platinum followed the silver into solution when their alloys were treated with nitric acid, the author investigated the properties of ten graduated alloys constituted as follows:—Series I, containing 12, 9 and 5 per cent. of platinum; series II, containing 2, 1·5, 1 and 0·75 per cent. of platinum; series III, containing 0·5, 0·4 and 0·25 per cent. of platinum. These alloys were prepared by fusion of the requisite proportions of silver and platinum under a gas-air blow-pipe flame in shallow porcelain cups, and then attacked by nitric acid of three different strengths, when it was found that the ordinary concentrated acid of 1·42 sp. gr., warmed, proved the best solvent, but that even under the most favourable conditions no more than 0·75 to 1·25, mean 1 per cent. of platinum, could be dissolved along with the silver.

When diluted nitric acid of 1·2 sp. gr. was employed, the maximum

amount of platinum taken up was only about 0·25 per cent.; whilst the highly concentrated acid of 1·50 sp. gr. proved altogether inappropriate, giving a bulky, insoluble product consisting of platinum black, intermixed with nearly the whole of the silver nitrate formed.

It would appear, then, that Berthier's account, quoted by Percy, and the statement in Bloxam's *Chemistry* are incorrect.

Discussion.

Mr. Vernon Harcourt suggested that the composition of the alloys of platinum and silver might vary with the temperature at which they were formed, and that Mr. Spiller should determine the solubility of alloys formed at higher temperatures than those he had employed.

Mr. Friswell thought that impurities in the nitric acid might account for some of the discrepant statements on record.

65. "Dalton's law in solutions. The molecular depression of mixtures of nonelectrolytes." By Meyer Wilderman, Ph.D.

Since Van't Hoff has shown that the generalisations arrived at by Boyle and Guy-Lussac in the cases of gases are equally applicable to dissolved substances in dilute solutions, the conclusion must be drawn that the third gaseous law, the law of Dalton, holds for dilute solutions also, this being a necessary consequence of the nature of osmotic pressure. Following up the thermodynamic considerations of Planck, the equations for mixtures of two or more electrolytes and the experimental proof of them are given.

66. "The action of bromdiphenylmethane on ethyl sodacetoacetate." By G. G. Henderson D.Sc., M.A., and M. A. Parker, B.Sc.

While bromtriphenylmethane and ethyl sodacetoacetate interact to give a disubstituted derivative, $(CPh_3)_2{:}CAc{\cdot}CO_2Et$, and ethyl acetoacetate, bromdiphenylmethane, on the other hand, appears to yield only a monosubstituted ester, *ethyl α-acetyl-β-diphenylpropionate*, $CHPh_2{\cdot}CHAc{\cdot}CO_2Et$.

This substance was prepared by heating bromdiphenylmethane (1 mol.) and ethyl sodacetoacetate (1 mol.) in presence of pure dry benzene or xylene till the reaction was completed, filtering from sodium bromide, concentrating the benzene solution, and purifying the crystals, which then separated, by recrystallisation from alcohol. It crystallises in shining, colourless needles, m. p. 85°, is sparingly soluble in alcohol but readily in benzene, and decomposes almost entirely when distilled.

On hydrolysis of this ester with cold dilute aqueous potash, a small quantity of *α-acetyl-β-diphenylpropionic acid*, $CHPh_2CHAc{\cdot}COOH$, was obtained in the form of extremely unstable crystals, which melt

about 90° and decompose at a slightly higher temperature. The salts of this acid are also very unstable. *β-diphenylethylmethylketone*, $CHPh_2 \cdot CH_2 \cdot CO \cdot CH_3$, was prepared by hydrolysing the ester with hot dilute alcoholic potash. It crystallises in colourless prisms which melt at 87·5° and distils with almost no decomposition at 315°. It is fairly readily soluble in alcohol, and very readily in benzene. The *oxime*, $CHPh_2 \cdot CH_2 \cdot C(CH_3) : N \cdot OH$, forms small, colourless crystals, m. p. 86—87°. It is sparingly soluble in alcohol but readily soluble in benzene. The *semicarbazone*, $CHPh_2 \cdot CH_2 \cdot C(CH_3) : N \cdot NH \cdot CO \cdot NH_2$, crystallises from alcohol in small, white clusters of minute crystals, which melt at 181°. It is sparingly soluble in alcohol and in benzene.

ADDITIONS TO THE LIBRARY.

I. *By Purchase.*

Behrens, H. Anleitung zur Mikrochemischen Analyse. Pp. xi + 224, mit 92 figuren im text. 8vo. Leipsig 1895.

Grandeau, L. Traité d'Analyse des Matières agricoles. 3rd edition. Tome I. Pp. viii + 560. Tome II. Pp. 614. 8vo. Paris 1897.

Griffen, R. B., and Little, A. D. The Chemistry of Papermaking, Pp. vi + 517. New York 1894.

Lewin, L. Lehrbuch der Toxikologie, zweite auflage. Pp. x + 509. Wien und Leipzig 1897.

Prior, Eugen. Chemie und Physiologie des Malzes und des Bieres. Pp. x + 597. Leipzig, 1896.

Stillman, T. B. Engineering Chemistry, a Manual of Quantitative Chemical Analysis. Pp. xxiii + 523. Easton, Pa., U.S.A., 1897.

Roth, E.; Heinzerling, C.; Helbig, Dr.; Goldschmidt, F.; Weyl, Th. Hygiene der Chemischen Grossindustrie. Pp. 629—910, mit 38 abbildungen im text. Jena 1896. (Vol. 8. Pt. 4 of Weyl's Handbuchs der Hygiene.)

Wiley, H. W. Principles and Practise of Agricultural Analysis. Vol. III. Agricultural Products. Pp. xii + 665. Easton 1897.

II. *Donations.*

Clarke, F. W. The Constants of Nature. Part V. A Recalculation of the Atomic Weights. New edition, revised and enlarged. Washington 1897. 8vo. Pp. vi + 370. From Smithsonian Miscellaneous Collections, 38. (Number 1075.)

Cohen, J. B. The Air of Towns. Washington 1896. 8vo. Pp. 41,

21 plates of illustrations. From Smithsonian Miscellaneous Collections, 39. (Number 1073.)

Duclaux, E. Atmospheric Actinometry and the Actinic Constitution of the Atmosphere. Washington 1896. 4to. Pp. iii + 48. From Smithsonian Contributions to Knowledge, 29. (Number 1034.)

Gray, Thomas. Smithsonian Physical Tables. Washington 1896. 8vo. Pp. xxxiv + 301. From Smithsonian Collections, 35. (Number 1038.)

Holden, Edward S. Mountain Observatories in America and Europe. Washington 1896. 8vo. Pp. vi + 77. From Smithsonian Miscellaneous Collections, 37. (Number 1035.)

McAdie, A. Equipment and Work of an Aero-physical Observatory. Washington 1897. 8vo. Pp. 30. From Smithsonian Miscellaneous Collections, 39. (Number 1077.)

Russell, F. A. R. The Atmosphere in Relation to Human Life and Health. Washington 1896. 8vo. Pp. 148. From Smithsonian Miscellaneous Collections, 39. (Number 1072.)

Varigny, Henry de. Air and Life. Washington 1896. 8vo. Pp. 69. From Smithsonian Miscellaneous Collections, 39. (Number 1071.)

From the Smithsonian Institution.

Griffiths, A. B. Respiratory Proteids Researches in Biological Chemistry. Pp. viii + 126. London 1897. From the Author.

RESEARCH FUND.

A meeting of the Research Fund Committee will be held in June. Applications for grants, accompanied by full particulars, should be sent to the Secretaries before June 8th.

LIST OF FELLOWS.

A new list of Officers and Fellows of the Chemical Society being in course of preparation, it is requested that Fellows will send any alteration of address, without delay, to the Assistant Secretary, Burlington House, London, W.

At the next meeting, on Thursday, June 3rd, the following Papers will be received. The authors of those marked with an asterisk have announced their intention of being present.

* "On the thermal phenomena attending the change of rotatory power of freshly-prepared solutions of certain carbohydrates; with some remarks on the cause of multirotation." By Horace T. Brown, F.R.S., and Spencer Pickering, F.R.S.

* "On the thermo-chemistry of carbohydrate-hydrolysis: (I.) The hydrolysis of starch by vegetable and animal diastase. (II.) The hydrolysis of cane-sugar by invertase." By Horace T. Brown, F.R.S., and Spencer Pickering, F.R.S.

* "Optical inverson of camphor." By Frederic Stanley Kipping, Ph.D., D.Sc., and William Jackson Pope.

* "Derivatives of camphoric acid. Part II. Optically inactive derivatives." By F. Stanley Kipping, Ph.D., D.Sc., and William Jackson Pope.

* "Racemism and Pseudoracemism. F. Stanley Kipping, Ph.D., D.Sc., and William Jackson Pope.

* "Note on some new gold salts of the Solanaceous alkaloids." By H. A. D. Jowett, D.Sc.

CERTIFICATES OF CANDIDATES FOR ELECTION.

N.B.—The names of those who sign from "General Knowledge" are printed in *italics*.

The following have been proposed for election. A ballot will be held on Thursday, June 17th.

Ackroyd, William,

9, Grandsmere Place, Halifax, Yorks.

Analyst. Public Analyst and Gas Examiner for Halifax. Fellow of the Institute of Chemistry, &c. Author of "The Old Light and the New; dealing with the Chemistry of Colour and the New Photography." During the last 20 years has published papers on Chemistry and Physics in the *Phil. Mag.*, *Chem. News*, *Proceedings* of the Phys. Soc. Lond., and the Royal Soc. Edin.

R. Meldola. Arthur Smithells.
Alfred H. Allen. A. G. Green.
C. Rawson. G. W. Slatter.

Walter Leach.

Barlow, Walter Harry,

152, Osbaldeston Road, Stoke Newington, N.

Analytical Chemist. Associate of the Institute of Chemistry. Certificated Student of Finsbury Technical College, 1890—95. Fourteen months Assistant Chemist at Gas Light and Coke Co.'s Works, Beckton. At present Assistant to Dr. Attfield, F.R.S.

R. Meldola. John Attfield.
R. C. T. Evans. J. Theo. Hewitt.

Arthur J. Chapman.

Brothers, William Malam,

Beechwood House, Prestwich, near Manchester.

Chemist. Studied Chemistry and Physics for the past six years at Bury Grammar School under Mr. W. French, M.A., F.I.C. For the past two years have been Chemist to Higher Clews Chemical Works, Rawtenstall. At present studying under Mr. French for the Honours Chemistry of South Kensington and Institute of Chemistry, and

desirous of obtaining the *Journal* for the current literature of the subject.

William French.	Edward Haworth.
Wm. Hesketh.	Christopher Wilson.

W. H. Barr.

Brown, Gerald Noël,

8, The Esplanade, Plymouth.

Analytical Chemist and Metallurgist. Associate of the Royal College of Science (Chemistry), 1894. Associate of the Royal School of Mines (Metallurgy), 1895.

Chapman Jones.	T. E. Thorpe.
W. Palmer Wynne.	Henry C. Jenkins.
Boverton Redwood.	W. C. RobertsAusten.

William A. Tilden.

Cameron, Ernest Stuart,

51, Pembroke Road, Dublin.

Demonstrator of Chemistry in the Royal College of Surgeons of Ireland, and Public Analyst for the County of Dublin.

Bernard Dyer.	James Dewar.
Alfred Smetham.	Otto Hehner.
Alfred Gordon Salamon.	*Boverton Redwood.*
Sydney Steel.	*J. F. H. Gilbard.*

Clutterbuck, Medwin Caspar,

61, Beaconsfield Villas, Brighton.

Lecturer on Chemistry to the Municipal School of Science and Art, Brighton. B.Sc. Lond., Ph.D. Strassburg, late Chemical Scholar of Un. Coll., Bristol. Joint Author with Prof. Fittig of an original research on tetrolic acid. Two years manager of Dallan Chemical Works, Burton-on-Trent. For the last three years Lecturer on Chemistry to the Municipal School of Science and Art, Brighton.

William Ramsay.	G. Harris Morris.
Sydney Young.	S. F. Dufton.

John Shields.

Cranfield, William,

5, Second Avenue, Halifax.

Teacher of Chemistry. Now and for several years past chief teacher of Chemistry at the Higher Grade Board School, Halifax. Studied at the Westminster Training College under S. Parrish, Esq., F.C.S., and at the Yorkshire College, Leeds.

Arthur Smithells.	John M. Thomson.
S. Parrish.	J. B. Cohen.

Herbert Ingle.

Gomess, A. F. Bilderbeck,

24A, Alfred Place West, South Kensington.

Medical. Late Assistant Pathologist, St. George's Hospital (including Pathological Chemistry). Passed final examination R.C.P., *i.e.*, the Medical portion of the Conjoint Scheme L.R.C.P., M.R.C.S. Gave demonstration at the International Congress (with Professor Delipine) for the prevention of air pollution with some of the products of combustion of coal.

Samuel Rideal. William Henry Walenn.
H. E. Roscoe. Frank Scudder.
Henry E. Armstrong.

Grundey, Frederick Roscoe,

20, Derby Road, Douglas, Isle of Man.

Science Teacher (Chemistry and Physics). Bachelor of Science (Vict.), Chemistry and Physics. Student in Owens College, Manchester, for 3 years. Teacher of Chemistry and Physics in the Organised Science School, Douglas, Isle of Man.

H. B. Dixon. E. Haworth.
A. Harden. W. H. Perkin, jun.
G. H. Bailey.

Halliwell, Edward,

Alexandra Crescent, Dewsbury.

Analytical Chemist and Associate of the Institute of Chemistry. Gained a Scholarship at the Yorkshire College, Leeds, for 3 years, 1891—4, and took full courses in Chemistry, Physics and certain Art Subjects. In 1894 passed the "Institute of Chemistry" examination for A.I.C., and have since been engaged in general analytical and chemical work in the laboratory of Mr. T. Fairley, Leeds.

Arthur Smithells. J. J. Hummel.
Wyndham R. Dunstan. Thomas Fairley.
Herbert Ingle. Julius B. Cohen.
Sydney Young. B. A. Burrell.

I rbord, Frank William,

Egham, Surrey.

Analytical Chemist. Assoc. R.S. Mines, Fellow of Institute of Chemistry. For 7 years Chemist to the Staffordshire Steel Co. Two years Chemist and Steel Works Manager to Messrs. Hatton, Sons & Co., Bilston, Staffs. For last 5 years Analytical Chemist to Indian Government, R.I. Engineering College, Cooper's Hill, Staines.

Herbert McLeod. Bennett H. Brough.
F. E. Matthews. W. R. Hodgkinson.
A. H. Church.

Harman, Harold,

Brewers Sugar Co., Greenock.

Chemist to Brewers Sugar Co., Greenock. Studied Chemistry at the Royal College of Science, South Kensington. Research Chemist in Mr. Lawrence Briant's Laboratory. Now Chemist to the Brewers Sugar Co., Greenock.

Lawrence Briant. — Arthur J. Starey.
Thos. Stevenson. — Cuthbert Vaux.
Chapman Jones. — *William Crookes.*
William Briggs.

Harrington, B. J.,

Montreal.

Professor of Chemistry McGill College, F.R.S.C., F.G.S., Ph.D., &c. Author of a number of original papers in the *Transactions* of the Royal Society of Canada, the *American Journal of Science* and others, more especially on the chemistry of rare and new minerals.

William A. Tilden. — W. C. Roberts-Austen.
William Ramsay. — *William Crookes.*
J. H. Gladstone.

Hunter, A. G. Kidston,

Colonial Mutual Buildings, Prince's St., Dunedin, N. Zealand.

Professor of Chemistry. Studied under the late Prof. Dittmar, Glasgow and West of Scotland Technical College. Author of "Examination of a Potable Water from a Bacteriological and Chemical point of view" (Paper read at Intercolonial Medical Congress, Dunedin, 1896). At present Professor of Chemistry in, and Principal of, Otago College of Pharmacy, Dunedin, New Zealand. Public analyst, &c.

James M. Mason. — John McArthur.
G. G. Henderson. — A. Humboldt Sexton.
James Robson. — *Matthew A. Parker.*

Johnston, George Lawson,

Kingswood, Sydenham Hill.

Director Bovril Limited. Attended Course Organic Chemistry Lectures, Royal College of Science, Kensington. Three years' analytical work under H. R. Gregory, F.I.C., and in private laboratory (analysis of foods particularly). Member of Chemical Industrial Society.

Playfair. — A. Searl.
Wm. Harkness. — S. Arch. Vasey.
James Dewar. — *R. Bannister.*
J. Woodward. — *C. Proctor.*

Mackenzie, John Edwin,

7, Ramsay Garden, Edinburgh.

Ph.D. (Strassburg), B.Sc. (Edin.) Assistant Professor of Chemistry, Heriot-Watt College, Edin. "Dimethoxydiphenylmethane and some of its Homologues." *Chem. Soc. J.*, 1896, 987. $\alpha\beta$- und $\beta\gamma$-Pentensäure," Liebig's *Annalen der Chem.*, **283**, 82. With A. G. Perkin, "Action of Nitric Acid upon Anthracene," *Chem. Soc. J.*, 1892, 865. With W. H. Perkin, jun., Ph.D., "Synthesis of Hexahydroterephthalic Acid," *Chem. Soc. J.*, 1892, 172. With F. S. Kipping, Ph.D., D.Sc., "Ethyl-*aa'*-Dimethyl-*aa'*-diacetylpimelate and some of its Decomposition Products," *Chem. Soc. J.*, 1891, 569.

Alex. Crum Brown. J. Gibson.
W. H. Perkin, jr. A. G. Perkin.
F. Stanley Kipping.

Pollock, William Robertson,

Kirkland, Bonhill, Dumbartonshire.

Assistant Manager in Turkey Red Dye-Work. Three years a chemical student in the Glasgow Technical College under Profs. Dittmar, Henderson, and Mills; engaged in a calico print works for 1½ years; for two years and at present on the staff of Messrs. Archibald Orr Ewing & Co., Dillichip; Bronze and Silver Medallist of the City and Guilds of London Institute.

Edmund J. Mills. G. G. Henderson.
A. Humboldt Sexton. R. R. Tatlock.
T. L. Patterson.

Scargill, Lionel Walter Kennedy,

14, Brunswick Place, West Brighton.

Schoolmaster. Honours in the Final School of Natural Science, Oxford. For the past year Science Teacher in the Langport Grammar School.

John Conroy. D. H. Nagel.
P. Elford. *W. W. Fisher.*
V. H. Veley.

Shenton, James Porter,

34, Lansdowne Road, West Didsbury, Manchester.

Analytical Chemist. A pupil of Messrs. Crace Calvert and Thomson, Royal Institution Chemical Laboratory, Manchester, from 1887 to 1890. Junior Assistant in the same laboratory from 1890 to June,

1894. Senior Assistant in the same laboratory from June, 1894, up to the present time.

William Thomson.	J. Carter Bell.
C. Estcourt.	P. Anderson Estcourt.
Alfred H. Allen.	*Charles E. Cassal.*
Otto Hehner.	*Thomas Fairley.*

Taverner, William,

1, Stapenhill Road, Burton-on-Trent.

Brewers' Chemist, in the employ of Messrs. Worthington & Co., Burton-on-Trent. I have for three years held the position of Chief Chemist to the above-mentioned firm, having previously worked for five years as Assistant Analyst in the Inland Revenue Laboratory, Somerset House. I received my chemical training first at the University College, Dundee, and afterwards at the Royal School of Mines, South Kensington, and the Somerset House Laboratory.

R. Bannister.	H. J. Helm.
E. Grant Hooper.	C. Proctor.
J. Woodward.	J. H. Robbins.

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PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

EDITED BY THE SECRETARIES.

No. 181. Session 1896–7.

June 3rd, 1897. Professor Dewar, F.R.S., President, in the Chair.

Messrs. Thomas Tickle and Thomas Girtin were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. John Ball, Ph.D., 18, Redshaw Street, Derby; Alec Alfred Beadle, Beadonwell, Belvedere, Kent; James Walter Horseman, 5, South Parade, Chelsea, S.W.; Charles John Jodrell Mansford, B.A., Lady Manners Grammar School, Bakewell, Notts.; Thomas Southern, jun., 2, Cherry Mount, The Cliff, Higher Broughton, Manchester; Francis Samuel Young, M.A., Mill Hill School, N.W.

Of the following papers, those marked * were read:—

***67. "On the thermal phenomena attending the change of rotatory power of freshly-prepared solutions of certain carbohydrates; with some remarks on the cause of multirotation." By Horace T. Brown, F.R.S., and Spencer Pickering, F.R.S.**

During an investigation of the thermal changes attending hydrolysis under enzyme action, whose results are described in the next paper, it became necessary to enquire whether the change in the multi-rotation of certain sugars is attended with any heat disturbance, as it is now well known that, at any rate, dextrose and maltose are liberated by hydrolysis in the "birotatory" state. The authors find that the changes of rotation experienced by dextrose, lævulose, and milk-sugar in passing from the optically unstable α- to the optically stable β-form, are accompanied by distinct thermal effects which, although taking

place slowly in the solutions under ordinary conditions, can be produced, like optical stability, almost instantaneously by the addition of traces of an alkali. A full account is given of the apparatus employed, of the method of experiment, and the nature of the corrections to be applied. In the cases of dextrose and milk-sugar, there is a liberation of heat accompanying the change of rotatory power; with lævulose there is a very decided absorption; and with maltose no thermal disturbance is recognisable. The following are the values obtained.

	Per gram of sugar.	Per gram-molecule.
Dextrose	+0·588 cal.	+106 cal.
Lævulose	−4·64 cal.	−835 cal.
Milk-sugar.....	+0·19 cal.	+ 34 cal.
Maltose	0	0

The authors discuss the various explanations which have been given from time to time to account for multirotation, and consider that their experiments favour the view that it is conditioned by chemical rather than physical causes, and that Fischer is probably correct in his suggestion that dextrose, for instance, in passing from the optically unstable to the optically stable modification in solution, passes from the aldehyde, $C_6H_{12}O_6$, to the heptahydric alcohol, $C_6H_{14}O_7$. They believe, however, that the analogy which Fischer suggested, of the change of a lactone into its acid, is less close than that afforded by the gradual change of acetic aldehyde, in contact with water, into ethylidene glycol where the CHO group becomes $CH(HO)_2$.

***68. "On the thermo-chemistry of carbohydrate-hydrolysis: (I) The hydrolysis of starch by vegetable and animal diastase. (II) The hydrolysis of cane-sugar by invertase." By Horace T. Brown, F.R.S., and Spencer Pickering, F.R.S.**

The attempts made to determine the thermal effects of hydrolysis have hitherto been confined to indirect methods, based on the heats of combustion of the hydrolysable substance and its products. Such methods, it is shown, cannot give results of any real value, as the thermal changes to be measured are considerably within the experimental errors of the combustion values.

The paper describes the results obtained by direct measurement of the heats of hydrolysis of starch and of cane-sugar. Lintner's soluble-starch was for the most part used, as there are certain mechanical difficulties in employing starch-paste in the calorimeter, owing to its viscidity. The hydrolytic agents used for starch were (1) malt-diastase, (2) pancreatic-diastase, (3) Taka-diastase, and (4) saliva. With malt

diastase, the heat of hydrolysis was found to be + 2·60 calories per gram of amylin converted into maltose. The amount of heat is proportional to the water fixed, and is independent of the molecular complexity of the amylin attacked. The breaking down of the starch-molecule prior to hydrolysis does not appear to be attended with any thermal disturbance.

With pancreatic-diastase, the heat liberated per gram of amylin hydrolysed amounts to + 1·8 cal., a value sensibly less than that deduced from the action of the malt-diastase. With Taka-diastase, the heat disturbance is still less than with the other two agents. The possible causes of these differences are discussed.

Cane-sugar was hydrolysed with invertase, and was found to give a thermal effect of + 11·21 cal. per gram of cane-sugar inverted when the products were in the optically stable β-form, and 13·34 cal. per gram at the moment of liberation of the products, *i.e.*, when they are in their "birotatory" or optically unstable form. It is the larger number which correctly represents the heat of hydrolysis of cane-sugar.

Discussion.

Mr. Pickering made a statement as to some additional work which had been done in connection with the subject since the paper had been sent in to the Society. The nature of the change produced by water on the sugars has been suggested to be the conversion of the aldehyde groups present into aldehydrol groups, an action which there is every reason to believe occurs in the case of acetic aldehyde itself, and experiments were, therefore, made to ascertain whether the action in the case of aldehyde exhibits the same peculiarity as in the case of the sugars, of being greatly accelerated by the addition of alkali. This was found to be the case, and the analogy of the two actions is, therefore, greatly strengthened. In both cases, also, the ammonia combines directly with the substance—the sugar or the aldehyde—with evolution of heat, but the results with aldehyde show that the formation of these compounds is not the cause of the hydrating effect of the alkali, for, although the alkali renders the hydration instantaneous, the formation of the aldehyde ammonia proceeds gradually, and with the quantities used is complete only after seven or eight minutes, the action evidently being independent of, and posterior to, the hydration. The accelerative action of the alkali on the hydration is probably due to its increasing the number of free molecules of water present in the liquid, by forming continually dissociating compounds such as NH_4OH, $NaOH{\cdot}xH_2O$, &c., and a free molecule of water would be a far more active hydrating agent than the average water aggregate constituting the bulk of liquid.

Mr. A. R. Ling said he was under the impression that Béchamp, and subsequently Tollens, were the first to point out that the multirotation of carbohydrates was correlated with thermic phenomena, but neither had made the exact measurements now presented. He wished to know if the authors had observed any change in the density of the solutions before and after the transition from the abnormal to the normal rotatory power.

Dr. Kipping said that although it seems to be generally understood that the phenomenon of birotation is not the result of a purely physical change, the assumption that it is due to the mere hydration of the aldehyde group might be objected to as involving the apparent contradiction that a very considerable change in specific rotation is brought about, not by increasing or diminishing the number of asymmetric carbon atoms in the molecule, but by merely altering to a comparatively slight extent the asymmetry of the groups already present. Important data in support of the chemical or hydration explanation of birotation were afforded, however, by some experiments made at the suggestion of Emil Fischer, as it had been found (Jacobi, *Ann.*, 1892, **272**, 170) that the rapidity of the formation of a hydrazone from a sugar which showed birotation varied with the time which had elapsed since the sugar had been dissolved.

Mr. Horace Brown, in reply, said that he believed Mr. Ling was mistaken in his statement that Béchamp or Tollens had done anything to correlate multirotation with thermic phenomena. So far as he knew, the only previous work on this subject was that of Berthelot, who had indirectly determined, for the solid state, the heats of transformation of α- and γ-dextrose into the β form.

Up to the present time, the authors had been unable to discover any change of density in solutions of multirotatory sugars.

Whilst fully admitting the force of Dr. Kipping's objections, it must be remembered that, so far as our knowledge goes at present, we are not justified in denying that comparatively small changes in the asymmetry of groups may be attended with a considerable change in rotatory power. The experiments of Jacobi are fully described in the paper, and are regarded by the authors as strongly confirmatory of their views.

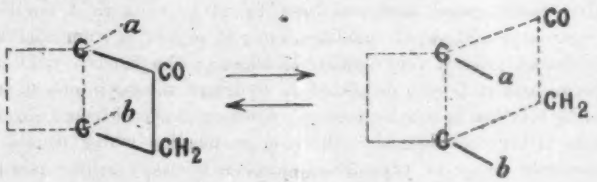
***69. "Optical inversion of camphor." By Frederic Stanley Kipping Ph.D., D.Sc., and William Jackson Pope.**

It was shown some time ago (Trans., 1893, **63**, 548) that two optically active isomeric sulphonic chlorides of the composition $C_{10}H_{15}O{\cdot}SO_2Cl$ could be obtained from the product of the action of anhydrosulphuric acid on ordinary *d*-camphor; these two compounds differed only in

optical and crystallographic properties, and it was therefore concluded that they must be regarded as optical antipodes.

This conclusion has been fully borne out by some recent work, in the course of which the properties of a considerable number of inactive compounds, prepared from inactive camphorsulphonic chloride, have been examined; it has thus been proved beyond doubt that these inactive compounds are composed of equal quantities of two enantiomorphous camphor derivatives, and that, consequently, either before or during sulphonation, the original *d*-camphor must be partly converted into its optical antipodes, *l*-camphor.

In the present paper, particular attention is drawn to this interesting case of optical inversion, as the intramolecular changes which take place appear to be entirely different from those which occur in the case of substances which contain asymmetric carbon atoms as constituents of an open chain. Although the constitution of camphor is still a matter for further investigation, it is now almost universally admitted that the skeleton of this substance consists of two closed carbon chains having two or more carbon atoms in common; further, a study of the chemical and optical properties of the various modifications of camphoric acid leads to the conclusion that each of the carboxyl groups in camphoric acid is united to an asymmetric carbon atom (Aschan, *Acta Soc. Scient.*, 21, [5], 1—227). Admitting these two apparently well-founded assumptions, the conversion of *d*- into *l*-camphor requires that part of one of the closed chains, for example, the group $-CH_2-CO-$, should change places with the two atoms *a* and *b* as shown in the following scheme.



As this view is based upon the two assumptions already stated, the matter is discussed from other standpoints, and it is finally concluded that the changes which occur in the optical inversion of camphor are of the nature already suggested.

***70. "Derivatives of camphoric acid. Part II. Optically inactive derivatives." By F. Stanley Kipping, Ph.D., D.Sc., and William Jackson Pope.**

The optically inactive, externally compensated derivatives of camphoric acid described in this paper were prepared initially from ordinary

d-camphor by first converting this substance into the approximately inactive camphorsulphonic chloride (Trans., 1893, **63**, 547) or camphorsulphonic bromide (Trans., 1895, **67**, 354), from which inactive π-chlorocamphor and racemic π-bromocamphor were then obtained by the method previously employed (Trans., 1895, **67**, 371).

Inactive π-chlorocamphoric acid, $C_{10}H_{15}ClO_4$, prepared by oxidising inactive π-chlorocamphor with nitric acid, crystallises in flat plates or in prisms, and melts at about 194—195°; its *anhydride*, $C_{10}H_{13}ClO_3$, melts at 193—194°.

Inactive π-bromocamphoric acid, $C_{10}H_{15}BrO_4$, obtained in a similar manner from racemic π-bromocamphor, is a crystalline powder melting at about 203—204°; its *anhydride*, $C_{10}H_{13}BrO_3$, melts at 155—156°.

These four externally compensated substances resemble the corresponding active compounds (Kipping, Trans., 1896, **69**, 913; Lapworth and Kipping, Trans., 1897, **71**, 1) very closely in general properties, but the inactive anhydrides are not easily obtainable in large crystals, active π-bromocamphoric anhydride forms large, monosymmetric crystals, measurements of which are given.

Inactive trans-*π-camphanic acid*, $C_{10}H_{14}O_4$, is obtained by the decomposition of the sodium salt of π-chloro- or π-bromocamphoric acid. It crystallises from water in monosymmetric prisms, which contain one molecule of water of crystallisation, but from ethylic acetate it is deposited in anhydrous, monosymmetric, six-sided plates; the anhydrous crystals change in crystalline form at about 130° and melt at 164—165°, namely, at the same temperature as the anhydrous active acid.

Active trans-π-camphanic acid (Trans., 1896, **69**, 929) has been further investigated, and has been found to exist in a number of different crystallographic modifications; it separates from cold water in hydrated prisms, very similar to those of the inactive acid in all respects, and it is also deposited in hydrated monosymmetric prisms from its solution in ethylic acetate; when crystallised from benzene, it affords either well-defined orthorhombic needles which contain one molecule of water of crystallisation, or a microcrystalline powder of the anhydrous acid, according to the conditions of the experiment. From a mixture of chloroform and light petroleum, it is deposited in large, transparent, anhydrous orthorhombic prisms which change in crystalline form at 100°.

The conclusions to be drawn from these and other facts bearing on the relation between the active and inactive trans-π-camphanic acids are discussed in the following paper.

Inactive cis-π-camphanic acid, $C_{10}H_{14}O_4$, is the principal product of the distillation of trans-π-camphanic acid. It crystallises in large, transparent, hexagonal plates, which are indistinguishable from those of the corresponding active acid (Trans., 1896, **69**, 943) except in optical

behaviour; the crystals of the active acid are circularly polarising and all of one kind, whereas those of the inactive substance show either right- or left-handed circular polarisation. It is thus possible to separate this externally compensated cis-π-camphanic acid into its *d*- and *l*-isomeric components.

Inactive trans-*camphotricarboxylic acid*, $C_{10}H_{14}O_6$, is obtained when inactive trans-π-camphanic acid is oxidised with nitric acid; it crystallises from water in lustrous transparent, monosymmetric prisms, which differ from those of the active acid (Trans., 1896, **69**, 951) deposited under similar conditions in being anhydrous, and consequently also in crystalline form. It melts at 224—225°, whereas the active acid melts at 196—197°.

Inactive trans-*camphotricarboxylic anhydride* forms transparent, monosymmetric crystals which are remarkably similar to those of the active anhydride; it melts at 253—254° whether heated alone or with an approximately equal quantity of the active substance.

***71. "Racemism and pseudoracemism." By F. Stanley Kipping, Ph.D., D.Sc., and William Jackson Pope.**

The data afforded by a comparison of the physical and crystallographic properties of the optically inactive substances described in the preceding paper with those of the corresponding active compounds (Trans., 1896, **69**, 913), and a number of other facts collected during the investigation of various active and inactive π-derivatives of camphor, have led the authors to the conclusion that the present classification of externally compensated substances into (*a*) mere mixtures and (*b*) racemic compounds, requires modification.

It has been found that optically inactive substances which are not mere mixtures of individual crystals of each of the enantiomorphous components are either very similar to, or extremely different from, their isomeric constituents in all those properties more immediately connected with crystalline structure; no intermediate degree of similarity is, in fact, observable in any case where these properties have been thoroughly examined.

Such externally compensated substances fall, therefore, into two groups. Those which closely resemble the corresponding active compounds are called *pseudoracemic*, the name racemic compound being reserved for those of the other group, of which racemic acid is the classical example.

The subdivision of optically inactive compounds has, not only an experimental, but also a theoretical basis. It can be shown that, in accordance with the present theory of crystalline structure, optically active and racemic compounds cannot assume the same type of homo-

geneous crystalline structure, but that an externally compensated substance may form crystalline individuals extremely similar to, but still not identical with, those of its active isomerides; in the latter case, the crystals consist of mere intercalations of those of the active modifications, and the non-identity is the result of the disturbance set up by intercalation. It is to these substances that the term pseudoracemic is applied.

Definitions of pseudoracemic and of racemic compounds based on these considerations are given, and some of the properties of the two classes of substances are then discussed. It is pointed out that the melting point of an externally compensated substance does not afford conclusive evidence as to its nature at ordinary temperatures, inasmuch as changes in crystalline form frequently occur with a change in temperature, and a mere mixture may become a racemic compound, and *vice versa* before the melting point is reached; numerous experiments are quoted in support of this view. It is also concluded that solubility determinations are valueless as a means of deciding between the three classes of externally compensated substances.

The properties of a number of inactive substances described by Aschan, Emil Fischer, Liebisch, Wallach, and others are briefly discussed, and reference is made to a recent paper by Walden, which deals with the characteristics of optically active and racemic compounds.

Discussion.

Dr. Bone enquired what was the practical criterion between a mixture of two optically active substances and a racemic compound proper, and whether there is any difference between the readiness with which the racemic and pseudoracemic forms can be resolved.

Dr. Kipping said that, in the majority of cases, it is very difficult to distinguish between mixtures and racemic compounds except by crystallographic examination, but Liebisch's rule, that the density of a racemic compound is different from that of its optically active isomeride, if confirmed by further experimental data, might be made use of in many cases. Theoretically a racemic compound would probably be resolved into its components less readily than a pseudoracemic substance, but when using the methods at present known for the separation of externally compensated substances, it seems improbable that any general difference in this respect would be noticed.

***72. "Note on some new gold salts of the Solanaceous alkaloids." By H. A. D. Jowett, D.Sc.**

When hyoscine hydrobromide and auric chloride are mixed, either in concentrated, dilute, neutral or acid solution, a red precipitate is

formed which can be crystallised from a hot aqueous solution acidulated with hydrochloric acid. On analysis, the salt is found to be an additive compound of auric chloride with hyoscine hydrobromide [B·HBr·$AuCl_3$]. When this experiment is conducted in the presence of a large excess of hydrobromic acid, a chocolate coloured precipitate is formed which can be recrystallised from hot dilute hydrobromic acid and forms chocolate coloured prisms, which, on analysis, prove to be the auribromide of the base [B·HBr·$AuBr_3$]. Even when excess of hydrochloric acid is present the aurichloride is not formed. The analogous compounds of hyoscyamine and atropine were formed by similar reactions and resemble the corresponding salts of hyoscine in chemical and physical properties.

Experiments were made to determine whether the bromaurichloride of formula B·HBr·$AuCl_3$ was an isomorphous mixture of aurichloride and auribromide, in view of the evidence adduced by Herty (*J. Am. C. S.*, xviii., 130) regarding the composition of the salt formed by mixing solutions of platinic chloride and potassium bromide ($K_2PtCl_4Br_2$). It was proved, however, that this view could not be adopted for the constitution of the gold salt, which must therefore be considered a true chemical compound.

***73. "Production of camphenol from camphor." By J. E. Marsh, M.A., and J. A. Gardner, M.A.**

The authors have described (Trans., 1897, 71, 285) the production of an isomeride of camphor, camphenol. This substance was obtained by the action of strong sulphuric acid on chlorocamphene, $C_{10}H_{15}Cl$. Camphenol is produced by the action of the same reagent on camphene dichloride, $C_{10}H_{16}Cl_2$, which is the immediate product of the action of phosphorus pentachloride on camphor. The same camphenol is apparently produced from both the isomerides of the formula $C_{10}H_{16}Cl_2$, obtained from ordinary camphor, and a satisfactory yield is obtained in both cases. The action of strong sulphuric acid on other chloro-derivatives of terpenes has been examined. In particular, turpentine dihydrochloride behaves in a manner very similar to the camphor derivative, but the nature of the product of the reaction has not yet been determined.

***74. "Preliminary note on the oxidation of fenchene." By J. A. Gardner and G. B. Cockburn.**

Fenchene prepared from the fenchone of fennel oil by a modification of Wallach's method was oxidised on the water bath by moderately dilute nitric acid (1 part strong acid to 1 part water). The oxidation was complete in three days. After distilling with steam, the acid liquid

was neutralised with sodium carbonate and extracted with ether, to eliminate some insoluble oily matter. The alkaline liquid was now acidified and repeatedly extracted with ether. On evaporating the ether, a syrup was obtained which gradually crystallised. The crystals were purified from oily matter by washing with chloroform, and after recrystallisation from water melted at 207°; they proved to consist of cis-camphopyric acid. The oily substance, separated by chloroform, was distilled under diminished pressure. A considerable amount of decomposition took place, and an oil and a solid distilled over. The solid was crystallised from alcohol, and proved to be camphopyric anhydride (m. p. 187°).

The yield of camphopyric acid was about 9—10 per cent. of the fenchene taken.

75. "Apiin and apigenin." By A. G. Perkin.

In a preliminary notice upon this subject (*Proc.*, 1897, **13**, 53), some derivatives and decomposition products of apigenin were described; these, together with an account of further work upon this colouring matter are included in the present paper. The formation of phloroglucol and parahydroxyacetophenone, as the principal products of the gentle action of alkali upon apigenin, have been confirmed, and it is now shown that, at 200°, protocatechuic acid, parahydroxybenzoic acid, and phloroglucol are obtained in the same way. These results confirm those of Gerichten (*Ber.*, 1876, **9**, 1124), except as regards the production of parahydroxyacetophenone, which is not mentioned by him. On methylation, apigenin forms a dimethyl ether, $C_{15}H_8O_3(OCH_3)_2$, yellow needles, m. p. 171—172°, which furnishes with alcoholic potash a potassium salt, decomposed by water, and with acetic anhydride a monacetyl derivative, $C_{15}H_7O_3(OCH_3)_2C_2H_3O$, colourless needles, m. p. 195—196°. The diethyl ether, $C_{15}H_8O_3(OC_2H_5)_2$, yellow needles, melts at 161—162°, and its monacetyl derivative, $C_{15}H_7O_3(OC_2H_5)_2C_2H_3O$, colourless needles, at 181—182°. As previously shown, apigenin contains 3 hydroxyl groups, consequently one is in the ortho-position to a carbonyl group. Decomposed with alcoholic potash, the dimethyl ether yields anisic aldehyde, anisic acid, and a phloroglucol derivative, ethylparahydroxybenzoic acid being formed from the diethyl ether under similar conditions.

These results, with the exception of the production of protocatechuic acid by means of alkali, point to a close relationship between apigenin and chrysin, $C_{15}H_{10}O_4$, the colouring matter of poplar buds, which yields on decomposition phloroglucol, benzoic acid, and acetophenone. It is probable that apigenin is a hydroxychrysin.

This suggested relationship is borne out by the dyeing properties of

the two colouring matters, which show a close similarity. The formation of protocatechuic acid from apigenin appears to be the result of an oxidising action, for there is no evidence of a catechol nucleus in this substance. Further experiments upon its constitution are in progress.

In the previous communication (*loc. cit.*), the author erroneously assigned the discovery of the glucosoidal nature of apiin and the preparation of pure apigenin to Gerichten, instead of to Lindenhorn (*Inaug. diss. Würzburg*, 1867).

76. "Rhamnazin." By A. G. Perkin and H. W. Martin.

Rhamnazin was isolated from Persian berries by one of the authors and J. Geldard (Trans., 1895, **67**, 496), and shown to be a quercetindimethylether. The present investigation was instituted to determine the position of the methoxyl groups. On methylation, it yielded quercetintetramethylether, and from this result and other experiments described in the paper, it evidently contains no methoxyl group in the phloroglucol nucleus in the ortho-position relatively to the carbonyl group. By fusion with alkali at 200°, rhamnazin yielded phloroglucol and protocatechuic acid, and digestion with boiling alcoholic potash gave vanillin, vanillic acid, and a non-crystalline phloroglucol derivative. Oxidised by air in alkaline solution, vanillic acid and a similar phloroglucol derivative were obtained. No free phloroglucol resulted from either of these decompositions. Taking into consideration that though the dyeing properties of rhamnazin are extremely feeble it must still be considered a colouring matter, these results indicate that it has the constitution of a rhamnetinmonomethylether.

77. "Experimental verification of van't Hoff's constant in very dilute solutions. By Meyer Wilderman, Ph.D.

In van't Hoff's thermodynamic argument, the solutions are assumed to be very dilute, and the same assumption is made in the deductions from it of Planck, Riecke, Lorentz, Bolzmann, and others. The experimental verification in dilute solutions of van't Hoff's law is therefore especially important. The freezing point method has been worked out with greater accuracy for the purpose of this investigation (Trans., 1895, **67**, 1; Lewis, "On the Real and Apparent Freezing Point and the Freezing Point Methods," *Proc. Royal Society*, 1896; *Zeitsch. für physik. Chemie*, 1896, **19**, 233).

The author has determined van't Hoff's constant in dilute solutions with thermometers graduated to $\frac{1}{100}$th and $\frac{1}{1000}$th of a degree respectively, simultaneously for a series of compounds, cane sugar, alcohol, urea, acetone, aniline, phenol, dextrose, resorcin, maltose, milk sugar, at

converging temperatures above and below the freezing points, using different parts of the scale of both thermometers. Small deviations only from the theoretical value of 1·87 are found, due to the different sources of experimental error, van't Hoff's constant being thus confirmed in dilute solutions.

78. "The isomeric dibromethylenes." By Thomas Gray, B.Sc.

This paper contains a record of an attempt to prepare the stereoisomeride of symmetrical dibromethylene. The following reactions are discussed: (1) the reduction of tribromethane by sodium ethoxide; (2) the union of acetylene with bromine; (3) the reduction of acetylene tetrabromide; and (4) the addition of hydrogen bromide to bromacetylene.

By the first of these methods, Tawildarow (*Ann.*, 1875, 176, 22) obtained, in addition to $CH_2{:}CBr_2$, a liquid boiling at 157° and having the formula $C_2H_2Br_2$. The author confirms the observation of Michael (*Amer. Chem. Journ.*, 1883, 5, 192), and finds that the only product of this reaction, under varying conditions of concentration, is $CH_2{:}CBr_2$ and he attributes Tawildarow's observation to the formation of bromacetyl bromide by oxidation during the process of distillation.

The product of three other reactions is shown to be in every case the same symmetrical dibromethylene (CHBr:CHBr), boiling at 110°. The author considers that the formation of this substance by the fourth method, and the probable instability of the *cis*-modification, which should result from the second reaction, point to the formula $\begin{matrix} H\cdot C\cdot Br \\ Br\cdot C\cdot H \end{matrix}$ as representing the structure of the symmetrical dibromethylene at present known.

At the next meeting, on Thursday, June 17th, there will be a Ballot for the election of Fellows, and the following Papers will be received. The authors of those marked with an asterisk have announced their intention of being present.

"The reduction of perthiocyanic acid." By F. D. Chattaway, M.A., and H. P. Stevens, B.A.

* "Molecular refraction of dissolved salts and acids." Part II. By J. H. Gladstone, D.Sc., F.R.S., and W. Hibbert.

* "On a space formula for benzene." By J. Norman Collie, Ph.D., F.R.S.

* "On the production of some nitro- and amido-oxypicolines." By A. Lapworth, D.Sc., and J. Norman Collie, Ph.D., F.R.S.

"The so-called hydrates of iso-propyl alcohol." By T. E. Thorpe, LL.D., F.R.S.

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PROCEEDINGS
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CHEMICAL SOCIETY.
EDITED BY THE SECRETARIES.

No. 182. Session 1896–7.

June 17th, 1897. Professor Dewar, F.R.S., President, in the Chair.

Mr. Samuel Pollitt was formally admitted a Fellow of the Society.

A Certificate was read for the first time in favour of Mr. Oscar Guttmann, 12, Mark Lane, E.C.

The following were duly elected Fellows of the Society:—William Ackroyd; Walter Harry Barlow; William Malam Brothers; Gerald Noël Brown; Ernest Stuart Cameron; Medwin C. Clutterbuck, B.Sc., Ph.D.; William Cranfield; A. Bilderbeck Gomess; Frederick Roscoe Grundey, B.Sc.; Edward Halliwell; Frank William Harbord; Harold Harman; B. J. Harrington, Ph.D.; John Edwin Mackenzie, B.Sc., Ph.D.; William Robertson Pollock; Lionel Walter K. Scargill, B.A.; James Porter Shenton; William Taverner.

Of the following papers, those marked * were read:—

***79. "Molecular refraction of dissolved salts and acids." Part II. By J. H. Gladstone, D.Sc., F.R.S., and W. Hibbert.**

The present paper is a continuation of a previous communication to the Society two years ago, under the same title (Proc., 1895, 11, 120). It is especially concerned in replying to the questions, "Has a salt the same molecular refraction whether it be in the crystalline state or in solution?" and "How far is any refraction change dependent on the solvent used?" The paper also gives some conclusions to which the data appear to lead.

In a table previously published (Trans., 1895, 67, 831), there were many comparisons between the specific refraction of solid salts and their value in solution, but no crystals were examined excepting those which had only one axis, or where the different indices were very near together. By adopting the method of Damien as suggested by Pope, we now add seventeen more cases having two or three indices of refraction. The observations are in accordance with the conclusions previously drawn,

the refraction of the salt in solution being in some cases greater, and in other cases smaller, than that of the crystallised body. The change of refraction however rarely, if ever, amounts to 4 per cent.

In making experiments on the effect of different solvents, we have examined nine salts and acids, including those published in 1870 (Trans., 1870, 23, 101). The first result is to show that the specific refraction of the substances dissolved in water does not generally differ much from the value yielded by solution in other solvents. If, however, we examine those substances which show a great change of refraction when deduced from different strengths of solution in water, the result is very striking. A comparison of hydrochloric acid when dissolved in water and in different alcohols and ethers, is shown in a diagram of curves. Whilst in water the specific refraction of the acid is raised in the first instance from about 0·300 to 0·386, and then gradually rises on dilution to 0·400, the acid dissolved in the different alcohols shows a lower starting point and a more gradual rise, in the following order: methyl, ethyl, amyl, and capryl alcohols; followed by a very low starting point in the case of ethyl ether, with an actual decrease on dilution, and by scarcely any change at all in the case of amylic ether.

In the case of lithium chloride, which gives in water a curve rising on dilution second only to that of hydrochloric acid itself, the solution in alcohol yields a curve very similar in character. Ferric chloride, which is the most striking instance of a great decrease in refraction occurring on dilution with water, shows also a decrease when it is dissolved in alcohol and acetic ether. Nitric acid, when mixed with water, shows a great change of specific refraction, but when dissolved in nitrobenzene shows little if any.

The authors express their growing conviction that neither the salt nor the solvent really changes its specific refraction, but that by their interaction some new product or products result, in quantities determined by the proportionate amount of the two original substances. The action may be one of dissociation or of association, or of some hitherto unrecognised redistribution. It is the changing proportion of this *tertium quid* which makes itself apparent by the changing specific refraction of the solution.

Discussion.

The President said that the Society was much indebted to Dr. Gladstone for this last addition to his great work on the refractive indices of chemical substances. He wished it were possible to determine directly the refractive index of fluorine, which seemed, from Dr. Gladstone's results with fluorine compounds, to possess the smallest refractive power of any of the elements.

Professor DUNSTAN asked whether the authors had considered the possible influence of the formation of the alkyl chlorides on the solutions of hydrogen chloride in alcohols.

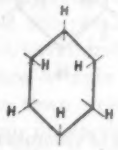
Dr. GLADSTONE, in reply, said they had been unable to detect the formation of any alkyl chloride in the solutions.

***80. "On a space formula for benzene." By J. Norman Collie, Ph.D., F.R.S.**

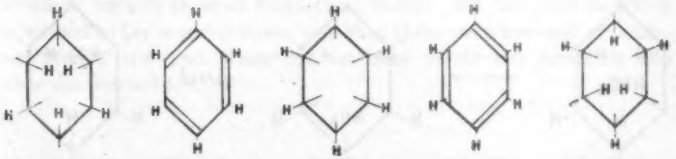
In this formula six tetrahedra (to represent the six carbon atoms) are arranged symmetrically in space equidistantly from a common centre, and so that they would occupy the six solid angles of an octahedron. They are connected also symmetrically with one another by single linkings. If the six hydrogen atoms (of benzene) are then arranged symmetrically on these tetrahedra, it will be found that there will be three on one side of the figure and three on the other side.

Movement in this arrangement might take place in two ways, a movement of each tetrahedron about its own centre, and a movement of each tetrahedron about the centre of gravity of the whole mass.

In the first case, simultaneous rotational movement of each tetrahedron about its centre would bring the combined hydrogen atoms towards the centre of the mass in *two distinct sets*; those on the 1, 3, 5 carbon atoms and those on the 2, 4, 6 carbon atoms, and a projection of this configuration might be expressed as follows:



In the second case, movement about the common centre would alter the relative positions of the tetrahedra with regard to one another, bringing into play the six unsaturated points of attraction on these tetrahedra. The projection of these different phases can be represented by the following formulæ:

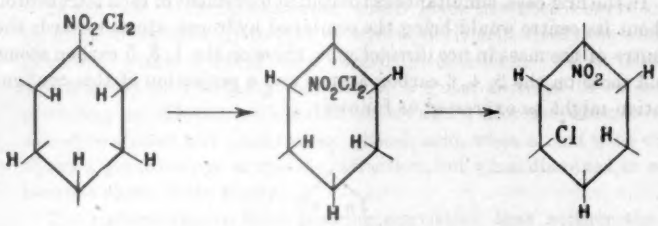


First phase. Kekulé's formula. Centric formula. Kekulé's formula. Last phase.

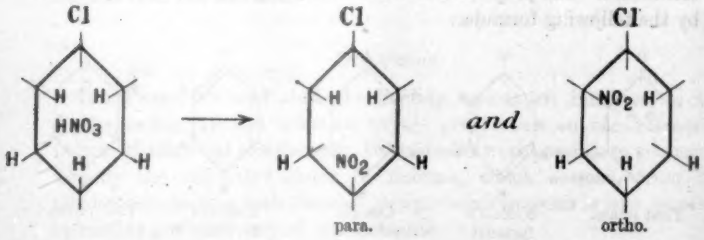
This space formula is therefore in complete accord with that of Kekulé and the centric formula, and shows how they are mutually convertible the one into the other. It also shows how the supposed double bindings in the Kekulé formula shift between the carbon atoms, thus rendering two orthochlorobenzenes impossible. But it differs from both, in that it shows how there may be two distinct sets of hydrogen atoms, and that when one set is inside the molecule, the other set is outside the molecule.

It can offer an explanation also of the fact that when one set of groups is present in a benzenoid compound, further substitution gives ortho- and para-diderivatives; whilst, when another set is present, on further substitution meta-diderivatives only are formed.

When chlorine acts on nitrobenzene, the chief product is metachloronitrobenzene. The nitro-group belongs to the group that favours the production of meta-diderivatives. This nitro-group, being in a sense unsaturated, might possess a certain amount of "residual affinity" which would be sufficient to attract the entering chlorine molecule, and direct it towards the hydrogen atoms that come to the centre at the same moment that it does itself.



On the other hand, in the case of chlorobenzene, if nitric acid be allowed to react with it, no such additive compound would be produced, and the attraction of the three hydrogen atoms attached to the other three carbon atoms might just be sufficient to determine its reaction with them.



Discussion.

Professor Tilden thought the paper a valuable contribution to the theory of the construction of the benzene molecule, though he felt doubtful about the validity of the division of the substituents into saturated and unsaturated, since this distinction was, in any case, not a sharp one.

Mr. Sworn considered that the formula proposed did not differ materially from the octahedral formula of Victor Meyer and others, nor did the explanation by the law of substitution now suggested differ substantially from one proposed by himself in a paper published in the *Philosophical Magazine*.

Dr. Kipping said he was not satisfied with the conclusion that three hydrogen atoms in benzene occupy different positions to the other three. If this were true then two monosubstitution derivatives become possible. From the readiness with which rings are formed from side groups, it would appear that the meta-position corresponds with the ortho-position.

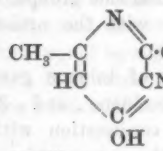
Mr. Friswell said that the ordinary nitration of toluene gave a mixture of about 65 parts of orthonitrotoluene and 35 of paranitrotoluene, or very nearly 2 to 1. In conjunction with Dr. T. A. Lawson he had endeavoured to alter these proportions. Every possible variation of temperature down to nitration at or near zero or as high as 40°, every variation of nitrating mixture from large proportions of sulphuric acid to the use of nitric acid alone, every variation in the order and rate of mixture, the nitration of toluene in which paranitrotoluene had been previously dissolved, had been tried. Yet no important variation of the proportions of the two products had been produced. Mr. A. G. Green had repeated these experiments, and confirmed them. The space formula now suggested by Dr. Collie afforded an explanation, since there were two orthohydrogen atoms during the rotation postulated inside the ring, and only one para-hydrogen atom in that condition. He had long considered this problem, and he had, in conjunction with Mr. C. Mills, commenced to experiment in order to ascertain whether the results might not be due to the existence of two isomeric toluenes.

Professor Collie, in reply, pointed out that the space formula for benzene which he had proposed was necessarily similar in many respects to others, notably those of Vaubel and Sachse; but the point on which he wished to lay especial stress was, that there were two sets of hydrogen atoms, and that when one set was inside the molecule the other set was outside.

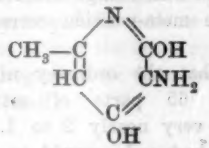
***81. "On the production of some nitro- and amido- oxypicolines." By A. Lapworth, D.Sc., and J. Norman Collie, Ph.D., F.R.S.**

When dioxypicoline (Trans., 1891, 59, 617) is warmed with 60 per cent. nitric acid, a nitro-compound is at once produced, $C_6H_7NO_2 + HNO_3 = C_6H_6N_2O_4 + H_2O$. This nitrodioxypicoline possesses all the properties of a nitrophenol, it is light yellow in colour, and forms salts with bases.

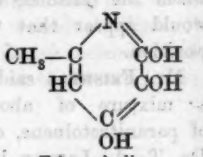
When it is carefully reduced with tin and hydrochloric acid, an amido-oxypicoline results, but should the temperature rise too high a secondary reaction occurs and a trioxypicoline is formed instead, (1) $C_6H_6N_2O_4 + 3H_2 = C_6H_6NO_2(NH_2) + 2H_2O$, (2) $C_6H_6NO_2NH_2 + H_2O = C_6H_6NO_2(OH) + NH_3$. The molecular constitution of these three compounds may be expressed by the formulæ:



Nitro-compound.



Amido-compound.



Trioxypicoline.

The amido-compound is remarkable for the series of brilliant colours it produces when treated with various oxidising agents: deep indigo-blue with ammonia and air, orange yellow with nitric acid, a deep moss green with alkaline ferricyanide of potassium, and a brilliant magenta with weak acetic acid and potassium bichromate. These colorations are very similar to those produced when various alkaloids are treated in a similar manner. This amido-oxypicoline forms salts with strong mineral acids but is also capable of liberating carbon dioxide from alkaline carbonates.

When its hydrochloride is only partially neutralised with sodium carbonate and the solution is boiled, an excessively insoluble substance separates, which seems to be a compound of the dioxyamidopicoline and the trioxypicoline, $2C_6H_6NO_2(NH_2) + H_2O = C_{12}H_{13}N_3O_4 + NH_3 + H_2O$. This insoluble compound by persistent boiling with strong hydrochloric acid is finally changed into the trioxypicoline and ammonia.

The trioxypicoline may be prepared at once from the dioxyamidopicoline hydrochloride, by using the full amount of sodium carbonate necessary to neutralise the hydrochloric acid, and then boiling for half an hour. It then crystallises out in long, needle-shaped crystals.

This trioxypicoline resembles pyrogallol in many of its reactions, it is an excessively powerful reducing agent, and in alkaline solution will develop photographs. It will precipitate silver from a solution

containing a considerable quantity of free nitric acid, and it also gives with oxidising agents a series of colour tests similar to those of the dioxyamidopicoline.

***82. "Further experiments on the absorption of moisture by deliquescent substances." By H. Wilson Hake, Ph.D.**

In a preliminary note (Proc., 1896, 12, 33) the author showed that certain deliquescent salts, when exposed to the air, attained a maximum of hydration, and that its maximum corresponded to a definite number of molecules in a large number of cases.

In the preliminary experiments no reference was made to the vapour-pressure of water in the air, but in experiments since made, the condition of the atmosphere as regards moisture has been carefully noted, or an artificially saturated atmosphere has been contrived under known conditions of temperature.

Having now experimented with 10 deliquescent chlorides (lithium, magnesium, cadmium, calcium, copper, nickel, cobalt, iron, manganese, and platinum), 3 nitrates (sodium, magnesium, and manganese) with sulphuric acid and with sodium formate, under various conditions, it was found that (1) they attract quantities of water corresponding in all cases to a definite hydrate, (2) after deliquescing to a maximum there followed in all cases a decline in weight and in four instances the salts returned to their original hydration and crystallised out, and that (3) the amount of hydration, though apparently always corresponding to a definite number of molecules of water, is not always the same, but seems to depend within certain limits both on the temperature and the relative humidity of the atmosphere and also on the conditions under which the air has access to the salt.

The author suggests that the above experiments demonstrate the phenomenon of deliquescence to be caused by hydration of the deliquescent salt.

***83. "The fusion point, boiling point, and specific gravity of nitrobenzene." By R. J. Friswell.**

Great discrepancies are found in the books as to the above constants.

Schultz gives in his first edition, 1882, 1·2002 at 0° and 1·1866 at 14·4°; in his second edition, 1·208 at 15°. Fusion point +3°.

Beilstein gives the same, and quotes Mitscherlich for the fusion point and Kopp for the specific gravity.

Gmelin gives 1·209 and +3°, and quotes Mitscherlich. As to boiling points, Gmelin, quoting Mitscherlich, gives 213°, Schultz, 1882, gives

210°; in 1886, 206—207°, Beilstein quoting Städeler, 205° at 730 mm.

It would thus appear that several of these numbers have been quoted unverified for over 60 years.

No statement of specific gravity of solid nitrobenzene has been published excepting that in *Watts' Dictionary*, given to A. G. Green in a private communication by R. J. Friswell. Determinations of the various points have been made. Calculated for comparison with water at 4° the sp. grs. are:

	t	d
Solid.....	1·5	1·3440
Liquid	3·8	1·2220
„	13·0	1·2160
„	28·0	1·1931

Boiling point corrected 209·0°.

Melting and solidifying point +5°.

Nitrobenzene is remarkable as having a distinctly coloured vapour very closely resembling that of chlorine. The colour is easily visible in a thickness of about 2 inches and is strongly marked when 6—8 inches are examined. The author is not aware of any other organic vapour of so simple a constitution which is visibly coloured.

No bands of absorption are shown in the visible spectrum when light is transmitted through this vapour. The violet and blue are absorbed as with the fluid but less strongly.

***84. "The action of light on a solution of nitrobenzene in concentrated sulphuric acid." By R. J. Friswell.**

Nitrobenzene is, as has long been known, readily soluble in concentrated sulphuric acid of 1·84 sp. gr. and upwards, but a comparatively small amount of dilution precipitates it and at about 1·7 the solubility is very slight.

When a solution in pure concentrated acid is exposed to light it slowly darkens. When exposed to direct sunlight, the darkening goes on with great rapidity, and in a few minutes the solution becomes quite black and opaque, then the action ceases. The light from burning magnesium produces the same effect.

The solution has been kept unchanged in the dark for upwards of four years. If the exposure to light takes place in a stoppered bottle, a slight odour of sulphurous acid is perceptible after some time in the air above the solution.

If the nitrobenzene thus used is recovered and redistilled and redissolved in sulphuric acid it behaves in exactly the same way.

Attempts were made to increase the change by spreading the solution on glass beads and between sheets of glass, but the depth of the colour of the product soon brought all change to an end.

Several hundred grammes of the black solution were prepared and attempts made to isolate the products of change, but though a brownish calcium salt was obtained and an ammonium salt in solution, the latter decomposed on evaporation with a caramel like odour; what was left was treated with phosphoric chloride, but no satisfactorily pure product could be obtained: the matter needs further investigation.

The rate of blackening of the solution is undoubtedly a measure of the actinic power of the light.

Discussion.

Mr. A. G. Green remarked on the possible similarity between the action of sulphuric acid on nitrobenzene in the presence of light, and the electrolytic reduction of a solution of nitrobenzene in sulphuric acid which had been investigated by Gattermann. In this case it was shown that at first phenylhydroxylamine, then paramidophenol was the product.

Dr. Hewitt said that he had noticed that coloration occurred in sulphonating nitrobenzene, even in the dark.

The President drew attention to the fact that in its changes of density near its solidifying point nitrobenzene appeared to show the same peculiarity as water, viz., an enormous change, but in an opposite direction. The action of light on the nitrobenzene solution in sulphuric acid was remarkable. If a flash of magnesium light were permitted to fall on the nitrobenzene solution through a quartz window, he thought that the blackening would furnish a good lecture illustration.

Mr. Friswell, in reply, said that he thought it quite possible that the change in the solution of nitrobenzene in sulphuric acid when exposed to light was of the same kind as that induced by electrolysis. He had never observed any coloration on sulphonating nitrobenzene when the materials were pure and light was excluded.

85. "The reduction of perthiocyanic acid." By F. D. Chattaway, M.A., and H. P. Stevens, B.A.

The atoms forming the molecule of perthiocyanic acid have been assumed to be arranged in a simple ring from the observation that on reduction it yields thiourea and carbon bisulphide. As, however, the properties of the substance render it probable that its molecule is larger than that represented by the simplest possible formula, $H_2N_2C_2S_3$, the conclusion that in this complex molecule all the structural units have a similar atomic arrangement is only valid if the amounts of thiourea and carbon bisulphide obtained on reduction approach those given by theory. The reduction of perthiocyanic acid has therefore been carefully carried out in various ways to determine the exact amounts of carbon bisulphide and thiourea obtainable and the nature and amount of any other products of the action.

When perthiocyanic acid is reduced by tin and hydrochloric acid, carbon bisulphide and thiourea are produced in almost theoretical amount, $H_2N_2C_2S_3 + 2H = CS(NH_2)_2 + CS_2$, only very small quantities of hydrogen sulphide and carbon dioxide are produced in addition, these being doubtless formed by the hydrolysis of a small portion of the perthiocyanic acid under the influence of the hydrochloric acid, $H_2N_2C_2S_3 + 2H_2O = CS(NH_2)_2 + H_2S + CO_2 + S$.

86. "The so-called hydrates of isopropyl alcohol." By T. E. Thorpe, LL.D., F.R.S.

Four hydrates of isopropyl alcohol are stated to exist; $2C_3H_8O \cdot H_2O$, isolated by Erlenmeyer in 1863; $3C_3H_8O \cdot 2H_2O$ and $3C_3H_8O \cdot H_2O$, discovered by Linnemann in 1865; and $C_3H_8O \cdot H_2O$, prepared by Ruhemann and Carnegie in 1888. All these hydrates boil within a comparatively small range—from 78° to 81°—whereas the amount of water they contain varies from 9 to 23 per cent.

The author gives reasons for doubting the existence of these hydrates as distinct chemical entities capable of definite isolation. By studying the behaviour of mixtures of isopropyl alcohol and water, it would appear that within certain fairly wide limits, water and the alcohol distil together in indefinite proportions, and that the water tends to pass over more rapidly than the alcohol, and hence is found in the largest proportion in the fractions of lowest boiling point. There is no evidence for the existence of these hydrates at their respective boiling points. Nor is there any more evidence for their existence at ordinary temperatures.

By synthetically forming them by the direct addition of the required amount of water to the alcohol, and allowing them to partially evaporate at the ordinary temperature of the air, it is found that the alcoholic strength of the residue is greatly increased; or, in other words, the water evaporates faster than the alcohol, although the latter boils 20° lower than the former. The two substances, therefore, are not in stable union, even at ordinary temperatures.

When the relative densities of the synthetically formed 'hydrates' are plotted in terms of the amount of water they contain, the values are found to lie on what is practically a straight line; or, in other words, the density of the mixture is, within the limits studied, very nearly a linear function of the amount of the constituents.

87. "The carbohydrates of the cereal straws." By C. F. Cross, E. J. Bevan, and Claud Smith.

This paper deals with the results of further investigations of the products of acid hydrolysis of the cereal straws and of the celluloses

isolated from them, including also the closely related esparto-cellulose. The results confirm those previously communicated (Trans., 1896, 69, 804—818), that the furfural-yielding constituents (furfuroids) are selectively attacked and for the most part (90 per cent.) dissolved; also from the exceptionally high numbers for cupric reduction, that they must exist in solution in a fully hydrolysed form (monoses).

The solutions when neutralised ferment with yeast; carbonic acid and alcohol are produced, and a proportionate effect upon the constants of the solution is shown (density, opticity, cupric reduction, and furfural). Under the conditions, the proportion of the celluloses fermented amounts to 30 per cent. of the total dissolved solids. Similar conclusions are deducible from a recent paper by Tollens (*J. für Landw.*, 1897, 106—107), in which the fate of malt-furfuroids in beer-fermentations is discussed. The experimental numbers in this paper show the disappearance of a large proportion of these constituents in the process.

Since the pentoses entirely resist alcoholic fermentation, as shown by Tollens (*Kohlenhydrate*, ii), and further confirmed by the authors, as well as by later observations of Tollens privately communicated, it is evident that the group of furfuroids thus fermented is constitutionally distinct from the pentoses.

Incidentally to observations on alcoholic fermentation with mixtures of known hexoses and pentoses, the authors find that the latter remain unaffected in presence of hexoses undergoing fermentation. Under certain conditions, however, the pentoses are removed from solution by the yeast organism; the necessary condition appears to be that of "starvation," in the sense, *i.e.*, of the absence of hexoses. The disappearance of the pentose under these conditions is indicated by determinations of furfural and the fall of the furfural numbers. This phenomenon appears to be the simple one of assimilation by the yeast organism, as shown by Bokorny (*Dingl. J.*, 1897, v, 303). The pentose undergoes constitutional change in such assimilation, as the yeast shows no increase in its normal small furfural number.

The authors further discuss the question of the constitution of furfuroids thus shown to yield to alcohol on fermentation, and conclude that the hypotheses of the existence of methylene ethers of the pentoses, or pentose formals, affords, up to the point arrived at, a consistent view of their differentiation from the pentoses.

The history of "piperonal," $C_6H_3\begin{cases}O\\O\\COH\end{cases}CH_2$, is cited in explanation of the exceptional difficulty of arriving at positive final proof of the analogous constitutional formula $C_5H_8O_3\begin{cases}O\\O\end{cases}CH_2$, which sums up the

above hypothesis in relation to the group of furfuroids in question. The instability of the pentose as compared with the aromatic residue prevents the application of reactions of resolution (Fittig) or synthesis (Wegscheider) such as have established the methylenic constitution of piperonal.

88. "Studies on the constitution of tri-derivatives of naphthalene No. 16. Conversion of chloronaphthalenedisulphonic acids into dichloronaphthalenesulphonic acids." By Henry E. Armstrong and W. P. Wynne.

In the course of their studies of naphthalene derivatives, the authors have had occasion to make great use of phosphorus pentachloride as an agent for displacing the SO_3H radicle by chlorine. It was therefore necessary to establish in every possible way the validity of this method of determining constitution in the naphthalene series, as it is obvious that the occurrence of isomeric change in any one case would materially weaken the force of all arguments based on its application.

With regard to the nature of the interaction, it is to be noted that, in a previous communication (Proc., 1895, 11, 83), it has been shown that it is usually possible to dispense with the pentachloride, and to obtain the chloronaphthalene corresponding with the given sulphonic chloride by merely heating the latter alone under appropriate conditions, but that as a rule the chloronaphthalene is obtained somewhat more readily and in larger relative amount when the pentachloride is used. In other words, the main function of the pentachloride is to promote the elimination of SO_2 from the SO_2Cl radicle.

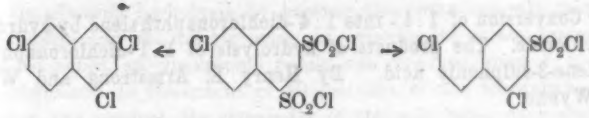
In the case of the chloronaphthalenesulphonic chlorides, the amount of dichloronaphthalene obtained by means of phosphorus pentachloride is relatively considerable, and the residue left after its removal from the crude product by distillation with steam yields nothing but the original chloronaphthalenesulphonic acid on hydrolysis.

The chloronaphthalenedisulphonic chlorides, however, behave somewhat differently, affording but a comparatively poor yield—rarely exceeding 30 per cent. of the theoretical amount—of trichloronaphthalene.

While preparing a full account of their work, the authors have felt it to be incumbent on them to thoroughly examine the residues left after separating the trichloronaphthalenes, which they have had occasion to produce on a large scale (Proc., 1895, 11, 86). Although, in view of the uniformity of the end-products, it was improbable that any change in orientation had taken place at the somewhat high temperatures at which the interactions were effected, it was obviously important to ascertain in every possible way whether such was the fact.

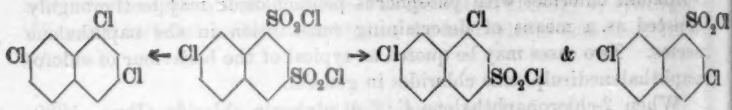
The results to be recorded are of interest, as they serve in every case to justify the conclusion previously arrived at, that the treatment of sulphonic chlorides with phosphorus pentachloride may be thoroughly trusted as a means of determining constitution in the naphthalene series. Two cases may be quoted as typical of the behaviour of chloronaphthalenedisulphonic chlorides in general.

When 2-chloronaphthalene-4′ : 2′-disulphonic chloride (Proc., 1890, 6, 129) is heated with the theoretical quantity of phosphorus pentachloride at 175° during 2 hours, it yields both 2 : 4′ : 2′-trichloronaphthalene and 2 : 4′-dichloronaphthalene-2′-sulphonic chloride in about equal proportions, about 50 per cent. of the material remaining unchanged. 2 : 4′-*Dichloronaphthalene-2′-sulphonic acid* affords a sparingly soluble *barium* salt, crystallising with $3\frac{1}{2}$ molecular proportions of water in microscopic needles; a sparingly soluble *potassium* salt, containing $1\frac{1}{2}$ molecular proportions, in thin scales; a *chloride* crystallising from benzene in small prisms melting at 156°; an *amide* crystallising from dilute alcohol in slender needles melting at 196°; and when the chloride is heated at 180—185° with phosphorus pentachloride it is converted into 2 : 4′ : 2′-trichloronaphthalene. On hydrolysing the chloride in sealed tubes with concentrated muriatic acid at 290°, or the potassium salt with a mixture of sulphuric and phosphoric acids and superheated steam, 2 : 4′-dichloronaphthalene is obtained. The course of change may therefore be thus represented:



When 2-chloronaphthalene-1′ : 3′-disulphonic chloride (Proc., 1890, 6, 13) is similarly heated with phosphorus pentachloride, it yields, besides 2 : 3′ : 1′-trichloronaphthalene, a somewhat larger proportion of a mixture of 2 : 1′-dichloronaphthalene-3′-sulphonic and 2 : 3′-dichloronaphthalene-1′-sulphonic (Proc., 1890, 6, 84) chlorides, about 50 per cent. of the material remaining unchanged. 2 : 1′-*Dichloronaphthalene-3′-sulphonic acid*, the isomeride present in the larger proportion, yields an anhydrous *potassium* salt, crystallising in thin, elongated scales, but exhibiting a tendency to separate in a gelatinous form; a *chloride* crystallising from benzene and light petroleum in small prisms melting at 130°; and an *amide* crystallising from dilute alcohol in slender needles melting at 218°. When the chloride is heated at 180—185° with phosphorus pentachloride, 2 : 1′ : 3′-trichloronaphthalene is formed. On hydrolysing the chloride in sealed tubes with concentrated muriatic acid at 290°, or the potassium salt mixed with sulphuric and

phosphoric acids, in superheated steam, 2 : 1′-dichloronaphthalene is obtained. The course of change may therefore be thus represented:



The other α-β-disulphonic chlorides behave similarly, the tendency being, however, as in the first of the above instances, to form only one of the two possible isomeric dichloronaphthalenesulphonic chlorides, no doubt because the SO_2 of the SO_2Cl radicle, like the SO_3H radicle, is more easily displaced from α- than from β-positions. It is not certain that these products are intermediate in the strict sense of the term, as the effect of prolonging the heating with phosphorus pentachloride at the minimum temperature at which the reaction takes place serves only to increase the yield both of the dichloro- and trichloro-derivatives. As the dichloronaphthalenesulphonic chlorides produced in these interactions decompose at temperatures a few degrees higher—10° to 15° in most cases—than those at which the corresponding chloronaphthalenedisulphonic chlorides from which they are obtained undergo change, it is not difficult to understand why they escape attack by phosphorus pentachloride under the conditions observed.

89. "Conversion of 1 : 1′- into 1 : 4′-dichloronaphthalene by hydrogen chloride. The products of hydrolysis of 1 : 1′-dichloronaphthalene-3-sulphonic acid." By Henry E. Armstrong and W. P. Wynne.

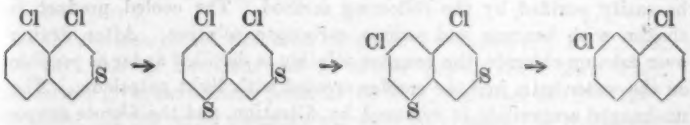
When 1 : 1′-dichloronaphthalene is heated with concentrated muriatic acid at 290°, it is wholly converted, save for a trace of carbonisation, into the isomeric 1 : 4′-dichloronaphthalene. This remarkable isomeric change does not seem to occur at temperatures below 200°, but is noticeable at 250°, and complete at 290°; it does not occur when 1 : 1′-dichloronaphthalene is heated either alone, or with water, or with concentrated phosphoric acid at 300°, but does happen when it is heated with sulphuric acid of a strength to cause considerable carbonisation. None of the isomeric dichloronaphthalenes show any tendency to change under these conditions.

The experiments which led to these results were made in consequence of the perplexing behaviour of 1 : 1′-dichloronaphthalene-3-sulphonic acid on hydrolysis. The isomeric α-sulphonic acid (Proc., 1890, 6, 81) requires only a temperature of 230° to effect its hydrolysis, and gives only 1 : 1′-dichloronaphthalene, whatever be the hydrolytic agent used; the β-sulphonic acid, on the contrary, is not hydrolysed below 285°, and

according to the agent used gives one or other of no less than three dichloronaphthalenes.

1 : 1′-*Dichloronaphthalene-3-sulphonic acid* is obtained in addition to about an equal proportion of 1 : 1′ : 3-trichloronaphthalene when 1-chloronaphthalene-1′ : 3-disulphonic chloride (Proc., 1890, 6, 16) is heated with phosphorus pentachloride at 160° (compare preceding abstract). It forms a sparingly soluble, anhydrous *potassium* salt crystallising in thin, elongated scales; a *chloride* crystallising from benzene in thin scales melting at 158°; an *amide* crystallising from dilute alcohol in short, slender needles melting at 197°; and 1 : 1′ : 3-trichloronaphthalene when its chloride is heated either with phosphorus pentachloride at 170°, or alone at 200—230°. On hydrolysing the potassium salt with dilute acids such as 1 per cent. sulphuric acid or 50 per cent. phosphoric acid at 290°, about 5—10 per cent. of the theoretical quantity of 1 : 1′-dichloronaphthalene is obtained, the residue being unchanged salt —a result by which the constitution of the acid is determined beyond doubt. When heated with 5 per cent. sulphuric acid or 60 per cent. phosphoric acid, carbonisation largely occurs, and with these and stronger acids a small amount of 1 : 4′-dichloronaphthalene is the only substance obtained, a better yield—some 20 per cent. of the theoretical—being got when the chloride is heated with concentrated muriatic acid at 290°. The production of 1 : 4′- instead of the expected 1 : 1′-dichloronaphthalene under these conditions is to be referred to the action of hydrogen chloride, either present or formed during the carbonisation of the salt.

On effecting hydrolysis by heating the potassium salt, mixed with sulphuric and phosphoric acids, in superheated steam instead of in sealed tubes, an unexpected result was obtained, pure 1 : 2′-dichloronaphthalene, to the extent of 40 per cent. of the theoretical amount, being the product, the remainder of the salt being carbonised. The explanation of this change has yet to be given. It is certain that the 1 : 2′-compound is not an intermediate step in the conversion of 1 : 1′- into 1 : 4′-dichloronaphthalene during hydrolysis in sealed tubes, both because it is unaffected by prolonged heating with concentrated muriatic acid, and because 1 : 2′-dichloronaphthalene-3-sulphonic acid cannot be detected in the material which has escaped hydrolysis, and, moreover, behaves normally on hydrolysis (compare preceding abstract). It is possible that, under the conditions specified, further sulphonation may precede hydrolysis, and that in consequence of the transference of chlorine to the para-position being thereby prevented, 1 : 2′-dichloronaphthalene is formed, thus:



Further experiments are being made to test this view.

Of the trichloro-naphthalenes, the 1 : 2 : 8-modification is the only one which undergoes change when heated with concentrated muriatic acid. Its sulphonic and disulphonic acids behave similarly, but the course of the action has not yet been worked out, owing to want of material.

90. "Note on the formation of diacetanilide." By George Young, Ph.D.

The introduction of a second acetyl group into acetanilide has been described in recent years by several authors. Kay (*Ber.*, 1893, **26**, 2853) treated acetanilide with acetyl chloride at 170—180° from 3 to 4 hours. Bistrzycki and Ulffers (*Ber.*, 1894, **27**, 91) heated a mixture of acetanilide and acetic anhydride, under pressure, 8 to 10 hours at 200—205°. Blacher (*Ber.*, 1895, **28**, 2356) boiled sodio-acetanilide suspended in xylene with acetic anhydride. Tassinari (*Gazz.*, 1894, **24**, i, 61) acted with acetyl chloride on sodio-acetanilide suspended in benzene. The English and German abstracts of Tassinari's paper state that this author also prepared diacetanilide by treatment of acetanilide with acetic anhydride, but the following quotations from the original paper show that the method used consisted in boiling a mixture of acetanilide, acetic anhydride, and sodium acetate on a reflux apparatus for some hours. In the introduction to his paper, Tassinari makes the general statement, "le diacidanilidi si formano anche con anidride acetica ed acetato sodico a ricadere." It is true that in describing the preparation of diacetanilide, he does not mention sodium acetate—"Trattando dell' acetanilide con anidride acetica, come è detto sopra per la formanilide . . . ," but the passage referred to runs: "Scaldando a ricadere per alcune ore un misto di formanilide, anidride acetica, ed acetato sodico. . . ." Further, in a later paper (*Gazz.*, 1894, **24**, i, 444) in which the work of Bistrzycki and Ulffers is quoted, no notice is taken of a statement by these authors (*loc. cit.*) that, although acetanilide undergoes some change when boiled for 2 hours with acetic anhydride, they were unable to obtain any pure product from the reaction.

The introduction of the second acetyl group takes place much more easily than might be imagined from the results quoted. If acetanilide be boiled with 2 to 3 times its weight of acetic anhydride for half an hour, over 75 per cent. is converted into the diacetanilide, which may be easily purified by the following method. The cooled product is shaken with benzene and sodium carbonate solution. After drying over calcium chloride, the benzene solution is distilled as far as possible on the water bath, and the residue treated with light petroleum. The unchanged acetanilide is removed by filtration, and the filtrate evapo-

rated. The residue solidifies on cooling to a crystalline mass, melting at 37—38°. A single recrystallisation, by extraction with cold light petroleum and evaporation of the extract, is sufficient to purify it for analysis, when it melts sharply at 38°.

0·1792 gave 0·4449 CO_2 and 0·1025 H_2O. C = 67·71 ; H = 6·35 %.
$C_6H_5N(COCH_3)_2$ requires C = 67·79 ; H = 6·21 per cent.

Part of the diacetanilide formed is probably hydrolysed by the treatment with sodium carbonate solution, but by working with not too large quantities, and performing the purification as rapidly as possible, a yield equal to the weight of acetanilide taken may easily be obtained.

91. "Derivatives of phenetol azo-phenols." By J. T. Hewitt, M.A., D.Sc., Ph.D., T. S. Moore and A. E. Pitt.

One of the authors has shown (*Ber.*, 1895, **28**, 799) that certain substitution derivatives of benzeneazophenol can form addition products with half a molecule of water, differing very sharply in colour and other physical properties from the corresponding anhydrous compounds. In order to obtain further knowledge of this subject, various series of substituted benzeneazophenols are being prepared and examined. This communication deals with ortho- and para-phenol azophenols, $C_2H_5O\cdot C_6H_4\cdot N{:}N\cdot C_6H_4OH$, the examination of the meta-derivative being deferred. When a paraoxyazo-compound does form an addition product with water, the addition of the latter can be most frequently brought about by dissolving the azo-compound in benzene and precipitating it by gaseous hydrogen chloride as a hydrochloride of the general formula, $X-N{:}N\cdot C_6H_4OH,HCl$, and decomposing this with water. Frequently the molecule of hydrogen chloride is thus replaced by a half molecule of water.

Orthophenetolazophenol was prepared according to the method given by Jacobson and F. Meyer (*Annalen*, 1895, **287**, 213). The melting point was found to be 128° C. (corr.), Jacobson gives 131° C. The *hydrochloride* melted between 124° and 129° C. On decomposition with water, the azophenol was regenerated; after air drying it melted at 127—128°. It may be assumed that no water had been added. In order to further characterise the azophenol, the two following derivatives were prepared.

Orthophenetolazophenylbenzoate, $C_2H_5O\cdot C_6H_4\cdot N{:}N\cdot C_6H_4\cdot O\cdot COC_6H_5$ light scarlet needles, m. p. 98° (corr.). *Orthophenetolazophenylbenzene sulphonate*, $C_2H_5O\cdot C_6H_4\cdot N{:}N\cdot C_6H_4\cdot O\cdot SO_2C_6H_5$, brilliant red needles, m. p. 83° (corr.).

Paraphenetolazophenol has been prepared by Riedel (*D. R. P.*, **48**, 453), and also by Jacobson and F. Meyer (*Ann.*, 1895, **287**, 215). The former gives the melting point as 104·5° C., the latter as 125—126°. The method of the latter chemists was used to prepare the compound.

The melting point was found to be 125° (corr.). The *hydrochloride* gave no very sharp melting point, beginning to melt at 131°, fusion not being complete until 154°. On treatment with water, a pale yellow powder is obtained melting at about 100°. The same substance may also be obtained by dissolving phenetolazophenol in glacial acetic acid, adding fuming hydrochloric acid, and pouring into water. After careful drying in air the substance melted at 104—109° C. Apparently this substance consists of equimolecular proportions of water and paraphenetolazophenol.

	Calc. $C_{14}H_{14}N_2O_2,H_2O$	Found.			Mean.
C	64·62	65·10	64·49	64·39	64·68
H	6·15	6·40	6·29	5·95	6·21

The following derivatives of paraphenetolazophenol have been prepared.

Paraphenetolazophenyl acetate, $C_2H_5O\cdot C_6H_4\cdot N{:}N\cdot C_6H_4\cdot O\cdot COCH_3$, yellow leaflets, m. p. 118° (corr.). *Paraphenetolazophenyl benzoate*. $C_2H_5O\cdot C_6H_4\cdot N{:}N\cdot C_6H_4O\cdot COC_6H_5$, small reddish brown crystals, m. p, 126° (corr.).

Paraphenetolazophenylbenzene sulphonate, $C_2H_5O\cdot C_6H_4\cdot N{:}NC_6H_4\cdot OSO_2C_6H_5$, large, pale yellow plates, m. p. 104° (corr.).

92. "δ-Ketopinic acid and camphoic acid." By W. S. Gilles and F. F. Renwick.

In the description first given of ketopinic acid (*cf.* Armstrong, Trans., 1896, 69, 1397), it was stated that the acid was optically inactive, even when prepared by oxidising the most active chlorocamphydrene (pinene hydrichloride) obtainable. As it was a matter of importance to determine whether the inactivity was an inherent property or due to compensation, the authors have applied Pasteur's method, and have succeeded in separating a dextrorotatory modification by fractionally crystallising the mixture of salts obtained by combining the inactive acid with strychnine. δ-Ketopinic acid has the same melting point as the "inactive" acid from which it is separated.

In their previous note (Proc., 1897, 14, 64) the authors have stated that when ketopinic acid is oxidised by permanganate it is converted into a tribasic acid resembling the camphoic acid described by Marsh and Gardner; they are now able to state that the product is camphoic acid, having obtained from it the cis- and trans-camphopyric acids and camphopyric anhydride of these chemists.

An amount of camphoic acid equal to 80 per cent. of the weight of the acid oxidised may be obtained by boiling ketopinic acid with a solution containing 50 per cent. of nitric acid and adding small quantities of stronger acid ($d = 1·42$) from time to time, as the action proceeds.

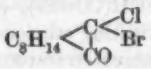
The authors will endeavour to ascertain if pinophanic and camphoic acids also exist in optically active forms, and what is the behaviour of active ketopinic acid on oxidation. Acids which are probably *cis*- and *trans*- forms of pinophanic acid have already been obtained.

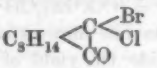
93. "Note on stereoisomeric di-derivatives of camphor, and on nitrocamphor." By T. M. Lowry, B.Sc.

Having learnt from Dr. Armstrong that, in the course of his early studies of camphor derivatives, he had observed that the substances obtained on the one hand by chlorinating bromocamphor and on the other by brominating chlorocamphor are apparently different, the author has submitted the two products to examination.

Brominated chlorocamphor, according to Cazeneuve, melts at 51·5°. The author finds that, on warming a mixture of chlorocamphor and bromine and once crystallising the product from spirit, well-defined crystals are obtained which melt at 53—55°; on analysis, these give results showing them to be bromo-chlorocamphor. By repeated recrystallisation from a variety of solvents, this product, however, may be resolved into two fractions, alike in composition, but widely different in specific rotatory power. The less soluble product, after being twenty-five times recrystallised, fused at 61°; its specific rotatory power was $[\alpha]_D = 16°$. The more soluble fraction—obtained by evaporating the mother liquor, distilling the residue with steam and recrystallising the product from dilute spirit—fused at 55°; its specific rotatory power was $[\alpha] = 63·9°$.

On directly chlorinating bromocamphor, an oil was obtained which could not be caused to crystallise; but a crystalline chlorinated bromocamphor was obtained without difficulty by heating bromocamphor with sulphuryl chloride at 130°. After being twice crystallised from spirit, the product fused at 56°; its specific rotatory power was $[\alpha]_D = 25·7°$ instead of 51°—the value observed in the case of the corresponding product from chlorocamphor. As in the former case, by repeatedly recrystallising this product, a less soluble fraction was separated melting at 61·5°, the specific rotatory power of which was $[\alpha]_D = 10·3°$; the more soluble fraction from the mother liquor had the specific rotatory power $[\alpha]_D = 28·3°$. There can be no doubt that the two products examined were *isomorphous mixtures* of constituents differing slightly in solubility but widely in specific rotatory power, careful study of the crystalline properties showing the constants to be nearly identical in the two cases. As both yield nothing but ordinary chlorocamphor on reduction, it follows that, in each case, the apparently simple product is a mixture of the two stereoisomeric *aa*-chlorobromocamphors:





These observations, in fact, undoubtedly afford the proof hitherto wanted, that in the ordinary derivatives of camphor containing halogens, the halogen atoms are both associated with the same carbon atom.

A careful examination both of ordinary dibromocamphor and of nitrobromocamphor has also been made, the result of which is that neither of these is resolvable into isomorphous constituents.

The author finds that when nitrobromocamphor is reduced by means of an alcoholic solution of potash, a nitrocamphor is obtained which has the properties attributed by Cazeneuve to that prepared from nitrochlorocamphor; the substance obtained by R. Schiff must have been impure. By the action of bromine on nitrocamphor dissolved in acetic acid, bromonitrocamphor is reproduced—not the compound $C_{30}H_{43}Br_2N_3O_{11}$, which, according to Schiff, is obtained on subjecting the potassium salt of nitrocamphor to the action of bromine.

Nitrocamphor appears to be a birotatory substance, its rotatory power in solution diminishing to a considerable extent as time proceeds —thus, a solution in benzene containing 10 per cent. of the substance, gave as initial value $[\alpha]_D = -112{\cdot}4°$, but after 3 hours $-102{\cdot}7°$, and at the expiry of 22 hours, when the rotatory power no longer changed, $-86{\cdot}5°$.

A further observation of interest has been made, viz., that when a solution of nitrocamphor in benzene is evaporated on the water bath, and the residue is further heated during about an hour, a product is obtained which is less soluble than the original nitrocamphor, and which melts at 190° instead of at 103°. The same substance is formed on heating fused nitrocamphor slightly above its melting point. The specific rotatory power of this substance in benzene (a 5 per cent. solution) is $[\alpha]_D = +187°$, and in chloroform $+167°$.

94. "The interaction of ethylene dichloride and ethylic sodiomalonate." By Bevan Lean, D.Sc., B.A., and Frederic H. Lees.

It has been shown by Prof. Perkin that, when ethylene dibromide is acted on with ethylic sodiomalonate, the chief product is 1 : 1-ethylic trimethylene dicarboxylate (208—210°, 760 mm.), thus: $\begin{matrix}CH_2Br\\ \cdot\\ CH_2Br\end{matrix} +$

$2CHNa(COOEt)_2 = \begin{matrix}CH_2\\ \cdot\\ CH_2\end{matrix}\!\!>\!C(COOEt)_2 + CH_2(COOEt)_2 + 2NaBr.$ In a later paper, he has shown that a small quantity of an oil of high melting point is formed, viz., ethylic butanetetracarboxylate (b. p. 240°, 40 mm.), and he has represented the action thus: $2(COOEt)_2CHNa + BrCH_2{\cdot}CH_2Br = (COOEt)_2CH{\cdot}CH_2{\cdot}CH_2{\cdot}CH(COOEt)_2 + 2NaBr.$ In later papers, he has shown that by substituting ethylene chloride for ethylene bromide the yield of ethylic butanetetracarboxylate can be

materially increased, and it has been proved by Bone and Perkin that the action is represented by the equation

$$(COOEt)_2CH_2 + \begin{matrix} CH_2 \\ | \\ CH_2 \end{matrix} > C(COOEt)_2 = (COOEt)_2CH \cdot \underset{\beta}{CH_2} \cdot CH_2 \cdot \underset{\alpha}{CH}(COOEt)_2.$$

The authors now show that at the same time small quantities of *ethylic butanetricarboxylate*, $(COOEt)_2CH \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot COOEt$ (b. p. 200—205°, 40 mm.) and *ethylic adipate* (b. p. 245°, 760 mm.) are formed. They attribute the formation of these two substances to the action of sodium ethoxide (or perhaps sodium hydroxide, since the materials cannot be entirely free from moisture) upon ethylic butanetetracarboxylate. It cannot be doubted that a similar action is of frequent occurrence, in greater or lesser degree, whenever substances containing two alkylic carboxylic groups attached to one carbon atom are treated with haloid compounds in the presence of sodium ethoxide. The following derivatives have been obtained from ethylic butanetricarboxylic acid. *Ethylic α-ethylbutanetricarboxylate*, $(COOEt)_2CEt \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot COOEt$, a colourless oil, b. p. 200—202°, 32 mm. Montemartini (Abstr., 1897, **72**, 19), has also prepared it; he gives the b. p. 205—208° at 35 mm. *α-Ethylbutanetricarboxylic acid*, $(COOH)_2CEt \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot COOH$, white crystals, m. p. 155—158°. Montemartini describes it as an oil. *α-Ethyladipic acid*, $COOH \cdot CHEt \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot COOH$, white crystals, m. p. 48—50° (Montemartini, 46—49°).

95. "Hexanaphthene and its derivatives. Preliminary note." By Emily C. Fortey, B.Sc.

In view of work now being carried on with respect to the naphthenes (Markownikoff, *Ber.*, 1897, **30**, 974, 1211, &c.; Zelinsky *Ber.*, 1897, **30**, 387, 1532), the author wishes to give a short account of some results as yet incomplete on hexanaphthene and its derivatives.

The substance was obtained from American light petroleum by fractional distillation with the aid of a long fractionating column made by Professor Sydney Young, and precisely similar to the one described by him (*Chem. News*, 1895, **71**, 177). Benzene and toluene were removed by prolonged treatment with a mixture of strong nitric and sulphuric acids. The hydrocarbon finally obtained (after 33 distillations) was not quite free from paraffins, but the purest fraction which boiled at 80·55—80·65° and had the specific gravity 0·7722 at 0°/0°, gave, on analysis, the following result as the mean of three determinations: C, 85·23; H, 14·60. Calculated for C_6H_{12}: C, 85·72; H, 14·28. The liquid boiling within 0·4 of a degree was chlorinated by means of a current of chlorine in presence of iron, and a mixture of di-, tri- and tetrachlorhexanaphthene was obtained. By the action of alcoholic potash on the fraction boiling at 135—140°

under a pressure of 30 mm., consisting chiefly of trichlor-hexanaphthene, hydrochloric acid was eliminated and the formation of a small quantity of benzene was proved by nitrating it and reducing the nitrobenzene to aniline, which gave the characteristic coloration with bleaching powder solution. Benzene having thus been obtained from hexanaphthene, the identity of the latter with hexamethylene is no longer questionable.

A small quantity of benzene hydrochloride, C_6H_7Cl, was also obtained by the action of alcoholic potash on trichlorhexanaphthene. It boiled at 135—140°, and an analysis gave the following result: C, 63·20; H, 5·91; Cl, 30·36. Calculated for C_6H_7Cl: C, 62·93; H, 6·12; Cl, 30·95. Hexanaphthene, when heated with fuming nitric acid, was found to be oxidised to adipic acid, as stated by Markownikoff (*Ber.*, 1897, 30, 975). As both this chemist and Zelinsky appear to have obtained methyl pentamethylene by the action of hydriodic acid on derivatives of hexanaphthene (*Ber.*, 1897, 30, 387, 1214), it became of interest to see whether the hydrocarbon itself would undergo isomeric change under similar conditions. Hexanaphthene boiling at 80·0—80·1° was therefore heated in a sealed tube with about five times its volume of hydriodic acid, sp. gr. 1·96, and a little amorphous phosphorus. The tube was heated to about 160° for 6 hours, from 250° to 270° for 3 hours, and was maintained at about 250° for 4 hours longer. The hydrocarbon, after being washed and dried, boiled almost constantly at 80°, showing that it was unchanged hexamethylene.

Zelinsky has found that methylhexamethylene is converted into dimethylpentamethylene by heating with hydriodic acid (*Ber.*, 1897, 30, 1532), it is therefore interesting to note that hexamethylene itself appears to be much more stable than its derivatives.

It is hoped to obtain a fresh supply of the substance by the fractional distillation of Galician petroleum, when the experiments will be continued.

ADDITIONS TO THE LIBRARY.

I. *By Purchase.*

Lafar, Franz. Technische mykologie, ein handbuch der Gärungsphysiologie Erster Band. Pp. xii + 362. Jena 1897.

Saare, O. Die fabrikation der Kartoffelstärke. Pp. xii + 577. Berlin 1897.

II. *Donations.*

Bedford, the Duke of, and Pickering, S. U. Report on the working and results of the Woburn Experimental Fruit Farm since its establishment. First Report. Pp. iv + 194. London 1897.

From the Authors.

Crookshank, E. M. A Text-book of Bacteriology, including the Etiology and Prevention of Infective Diseases. Fourth edition. Pp. xxx + 715. London 1896. From the Author.

Hantzsch, M. A. Précis de Stéréochimie. Pp. 223. Paris 1896. From the Publishers.

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PROCEEDINGS
OF THE
CHEMICAL SOCIETY.

EDITED BY THE SECRETARIES.

No. 183. Session 1896–7.

The following are the abstracts of papers received during the vacation, and published in the Transactions:—

98. "The ethers of camphoroxime." By M. O. Forster, Ph.D.

The *methyl ether* of camphoroxime boils at 181·5—182·5° under a pressure of 357 mm.; it has the sp. gr. = 0·9631, and the specific rotatory power $[\alpha]_D = -13·05°$ at 20°. It does not reduce an ammoniacal solution of silver nitrate, and dissolves in mineral acids without undergoing change. The *nitrate* crystallises from benzene in needles melting at 81—82°, and has $[\alpha]_D = -16·9°$ in benzene; the *hydriodide* is amorphous, and melts at 157° with vigorous effervescence.

The ethyl ether (Nägeli) boils at 185° under a pressure of 336 mm., and has the sp. gr. = 0·9470; the specific rotatory power $[\alpha]_D = -19·0°$ at 23·5°.

The *benzyl ether* is a colourless oil, which on distillation is in part resolved into benzaldehyde and camphorimine, as represented by the equation $C_{10}H_{16}{:}NO{\cdot}CH_2{\cdot}C_6H_5 = C_{10}H_{16}{:}NH + C_6H_5{\cdot}CHO$; it has $[\alpha]_D = -16·4°$ in alcohol, and forms an amorphous *hydriodide* which melts at 91°. Concentrated sulphuric acid resolves the ether into camphoroxime and the resinous hydrocarbon, $C_{14}H_{12}$, obtained on dissolving benzylic alcohol in concentrated sulphuric acid. Alcoholic hydrochloric acid eliminates α-benzylhydroxylamine from the ether; the *platinochloride* of this base forms golden-yellow scales, and does not melt below 250°.

The *acetyl* derivative of camphoroxime is a colourless liquid, and is completely converted into acetic acid and campholenonitrile on distillation; it has the specific rotatory power $[\alpha]_D = -45·8°$ in alcohol, and on treatment with cold phenylhydrazine yields symmetrical acetylphenylhydrazine and camphoroxime.

The *benzoyl* derivative crystallises from acetone in magnificent six-sided prisms, and melts at 88—90°; it has $[\alpha]_D = -40{\cdot}7°$ in alcohol, and yields benzanilide when heated with aniline. Cold phenylhydrazine gives rise to benzoylphenylhydrazine and camphoroxime. *Camphoroxime hydrobromide* melts and evolves hydrogen bromide at 174°; it has $[\alpha]_D = -35{\cdot}8°$ in alcohol, and is converted by glacial acetic acid into campholenonitrile and hydrogen bromide. *Camphoroxime platinochloride* crystallises in transparent prisms which become opaque in the desiccator, and melts at 156·5° with vigorous effervescence; cold water regenerates the oxime. *Inactive camphoroxime* melts like the active modification at 118°; it crystallises from petroleum in diamond-shaped plates, and is racemic according to the classification recently suggested by Kipping and Pope (this vol., 135).

97. "The action of nitrogen trioxide and tetroxide on alcohols. Part I." By Julius Berend Cohen, Ph.D., and Harry Thornton Calvert, B.Sc.

The authors have found that when nitrogen trioxide or tetroxide dissolved in chloroform is allowed to act upon benzyl alcohol, that water is in both cases eliminated, and compounds of the formula $C_6H_5CHN_2O_3$ and $C_6H_5CHN_2O_4$ are probably formed, which rapidly decompose on standing into benzaldehyde, with the separation in the first case of nitric oxide, and in the second of nitrogen trioxide, according to the following equations, (1) $C_6H_5CHN_2O_3 = C_6H_5COH + 2NO$, (2) $C_6H_5CHN_2O_4 = C_6H_5COH + N_2O_3$. The latter substance, which may be termed benzylidene nitrosate, is decomposed by water into a compound of the formula $C_7H_7NO_3$, which is probably identical with a substance obtained by Lippmann and Hawliczek (*Ber.*, 1876, **9**, 1463) by the action of nitric acid upon benzaldehyde. By the action of reducing agents it is converted into benzyl alcohol, benzylamine and ammonia.

98. "The action of nitrogen tetroxide on ortho- and para-nitrobenzyl-alcohol." By Julius B. Cohen, Ph.D., and William H. Harrison, B.Sc.

The authors have discovered a simple method for preparing the aldehydes corresponding to ortho- and para-nitrobenzylalcohol. The reaction consists in treating the alcohol with a small quantity of nitrogen tetroxide in presence of air. A nearly theoretical yield of these aldehydes, hitherto very difficult to prepare, has been effected by this method.

99. "The action of aromatic amines upon diacetyltartaric anhydride." By Julius Berend Cohen, Ph.D., and William Hudson Harrison, B.Sc.

In attempting to prepare the isomeric toluido-acetyl tartaric acids, by acting upon diacetyltartaric anhydride with the isomeric toluidines, with a view to comparing their optical characters, the authors were unsuccessful; but obtained, on the other hand, by this reaction with different aromatic amines, a series of golden-yellow crystalline compounds. The formula of the aniline compound is probably $C_{16}H_{12}N_2O_3$, that of the paratoluidine compound $C_{18}H_{16}N_2O_3$, and of the *a*-naphthylamine compound $C_{27}H_{16}N_2O_3$. The constitution of these compounds has not yet been ascertained. The reaction in all cases is very complex, and the yield of the yellow substances very small.

100. "Studies on citrazinic acid. Part V." By W. J. Sell, M.A., and F. W. Dootson, B.A.

This investigation was commenced with the view of obtaining some evidence of the positions of the hydroxyl groups in citrazinic acid, by preparing the corresponding dichlorisonicotinic acid, and then replacing the chlorine atoms either by cyanogen or methyl, and thus by well-known methods obtaining one of the tricarboxy-acids whose constitution has been established. In the preparation of the dichlorisonicotinic acid by the interaction of phosphorus pentachloride on citrazinic acid, however, such a number of interesting substances were found to be produced that it was determined to publish this part of the work at once, leaving the remainder for a further communication. The following substances—amongst others—have been isolated, and are described in the paper.

(1) Chlorhydroxyisonicotinic acid; (2) dichlorisonicotinic acid; (3) tetrachlorisonicotinic acid chloride; (4) $a\beta a'\beta'$-tetrachlorisonicotinic acid; (5) tetrachlorpyridine; (6) pentachlorpyridine; (7) pentachlorpicoline.

101. "The condensation of choral with resorcinol. II." By J. T. Hewitt, M.A., D.Sc., and Frank G. Pope.

In an earlier paper (Trans., 1896, **69**, 1265), the view was expressed that the substance of the formula $C_{14}H_{10}O_5$, obtained by the condensation of choral hydrate with resorcinol, was a lactone of 2:4:2′:4′-tetrahydroxydiphenylacetic acid. The authors had overlooked a paper by Michael and Comey (*Amer. Chem. Journ.*, 1883—4, 5, 350) in which

the formula $C_8H_6O_3$ was attributed to the compound in question. The determination of the molecular weight by the lowering of freezing point of a phenolic solution gave as result 232; the values required by the formulæ $C_8H_6O_3$ and $C_{14}H_{10}O_5$ being 150 and 258 respectively. The analyses of the acetate and benzoate have further confirmed the authors' views that the compound possesses three hydroxyl groups. In addition to this, it has been found that a red salt is precipitated when an excess of sodium ethylate solution is added to an absolute alcoholic solution of the lactone: the salt was found to contain 22·10 per cent. of sodium, whilst the formula $C_{14}H_7O_5Na_3$ requires 21·30 per cent. of sodium.

The analysis of the salt, obtained by boiling the lactone with water and barium carbonate, led to the formula $Ba(C_{14}H_{11}O_6)_2$; the soluble zinc salt obtained in a similar way, gave a percentage of zinc which agrees with the formula $Zn(C_{14}H_{11}O_6)_2$.

102. "On β-oxycellulose." By Benjamin Samuel Bull, M.A., B.Sc.

β-Oxycellulose has been studied by several workers, and Cross and Bevan have prepared a trinitro-derivative. In this paper a benzoate and nitrate obtained from β-oxycellulose are described. These compounds are probably hexa-derivatives of a substance having the empirical formula $C_{16}H_{27}O_{14}$.

103. "A new synthesis of phloroglucinol." By David S. Jerdan, B.Sc.

When finely divided sodium is dissolved in a benzene solution of ethylic acetone-di-carboxylate and the solution is boiled for some hours, a gummy deposit is slowly formed. The whole is then shaken with water and the aqueous solution, after separation of the benzene, is acidified with sulphuric acid. The solution becomes milky and a granular precipitate falls after a short time. The new substance may be recrystallised from glacial acetic acid, and then possesses a composition corresponding with the formula $C_{12}H_{10}O_7$.

This compound, when boiled with methylic alcohol containing 3 per cent. of hydrogen chloride, took up a molecule of alcohol, giving a crystalline ester, $C_{13}H_{14}O_8$. The substance $C_{12}H_{10}O_7$ must therefore be a lactone. Further, on hydrolysis with baryta solution, the lactone gave carbon dioxide, alcohol, malonic acid, and phloroglucinol. The new compound is therefore a phloroglucinol derivative.

It is probably formed according to the equation:—$2C_{10}H_{14}O_5 + 3Na = C_{12}H_{10}O_7 + 3NaOC_2H_5 + 3H$. The immediate product of the reaction must of course be a sodium derivative, the lactone $C_{12}H_{10}O_7$ being formed from this on addition of sulphuric acid.

104. "Phenanthrone." By Francis R. Japp, F.R.S., and Alexander Findlay, M.A., B.Sc.

Phenanthrone was regarded by its discoverer, Lachowicz (*J. pr. Chem.*, 1883, [2], **28**, 173), as a ketone of the formula $\begin{matrix}C_6H_4\cdot CH_2\\ C_6H_4\cdot CO\end{matrix}$ Japp and Klingemann (Trans., 1893, **63**, 770) suggested that it might be a phenol of the formula $\begin{matrix}C_6H_4\cdot CH\\ \|\\ C_6H_4\cdot C\cdot OH\end{matrix}$ (*β-phenanthrol*).

In the hope of deciding between these two formulæ, the present authors have prepared various derivatives of phenanthrone. The evidence, however, points in both directions. The compound reacts both in the ketonic and in the phenolic form, although more frequently in the latter. In the great majority of its reactions it is a strict analogue of β-naphthol.

In preparing phenanthrone by the method discovered by Japp and Klingemann—reduction of phenanthraquinone with hydriodic acid—the authors find that two other substances are simultaneously formed: *β-phenanthrylic oxide* $(C_{14}H_9)_2O$ (m. p. 210°), and *tetraphenylenefurfuran* $\begin{matrix}C_6H_4\cdot C\text{—}C\cdot C_6H_4\\ \|\quad\quad\|\\ C_6H_4\cdot C\cdot O\cdot C\cdot C_6H_4\end{matrix}$ (m. p. 306°). The latter was obtained by Japp and Klingemann by the destructive distillation of monacetyl phenanthraquinol.

Phenanthrone and β-phenanthrylic oxide both yield molecular compounds with picric acid, $C_{14}H_{10}O,C_6H_2(NO_2)_3OH$ (m. p. 185°) and $(C_{14}H_9)_2O,2C_6H_2(NO_2)_3OH$ (m. p. 148°).

Phenanthrone, when in solution, is converted by aërial oxidation into the compound $C_{28}H_{18}O_3$ (obtained by another process by Japp and Klingemann), which crystallises in dark-red laminæ melting at 156—157°. This compound is broken up by acetic anhydride into phenanthrone and phenanthraquinone, the former undergoing acetylation. It may be synthesised by the direct union of phenanthrone and phenanthraquinone. The authors regard it as an aldol condensation compound of these two substances, and ascribe to it the constitution $\begin{matrix}C_6H_4\cdot C(OH)\cdot CH\cdot C_6H_4\\ C_6H_4\cdot CO\quad\quad CO\cdot C_6H_4\end{matrix}$. On boiling with fuming hydriodic acid, it is converted quantitatively into tetraphenylenefurfuran. Acetic anhydride converts phenanthrone into *β-phenanthrylic acetate*, $C_{14}H_9\cdot O\cdot C_2H_3O$ (m. p. 77—78°). When heated with methylic alcohol and sulphuric acid, phenanthrone yields *methylic β-phenanthrylic oxide*, $C_{14}H_9\cdot O\cdot CH_3$ (m. p. 96—97°). When heated with ammonia it yields a mixture of *β-phenanthrylamine*, $C_{14}H_9\cdot NH_2$ (m. p. 139°), and β-diphenanthrylamine, $(C_{14}H_9)_2NH$ (m. p. 237°). With phenylhydrazine at 200° it interacts,

eliminating water and ammonia and yielding 2′:3′-*diphenyleneindole* (m. p. 188—189°).

105. "The yellow colouring principles of various tannin matters. IV." By A. G. Perkin.

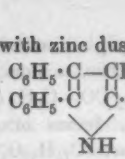
Cape sumach, the leaves of the *Colpoon compressum*, is used in South Africa as a substitute for sumach (*Rhus Coriaria*) under the name of "Pruim-bast." According to H. Procter (private communication) it contains 23 per cent. of a catechol tannin. Its dyeing property is due to the presence of a new glucoside, *osyritrin*, $C_{27}H_{30}O_{17}$, pale yellow needles, m. p. 185°, which is decomposed by acid into quercetin and glucose, $C_{27}H_{30}O_{17} + 2H_2O = C_{15}H_{10}O_7 + 2C_6H_{12}O_6$. This is not identical with viola-quercetrin (Mandelin, *J.*, 1883, 1369), $C_{42}H_{42}O_{24}$ which exists in the *Viola tricolor florensis*. The tannin, obtained as an orange-coloured, transparent mass, is a glucoside yielding, with acid, an anhydride or phlobophane and a sugar. By fusion with alkali, protocatechuic acid is formed. A re-examination of gambier catechu (*Ungarica Gambier*) corroborated the statement of Löwe (*Zeit. anal. Chem.*, 1874, 12, 127) that this contains quercetin. Acacia catechu not previously examined was found to contain the same colouring matter.

The dyeing properties of a commercial sample of Venetian sumach (*R. Cotinus*) are due to myricetin and not quercetin as stated by Löwe (*loc. cit.*). This result will be corroborated by the examination of a specially picked sample.

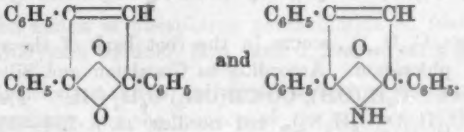
Valonia (*Quercus Ægilops*), divi-divi (*Cæsalpina Coriaria*), myrabolans (*Terminalia chebula*), agarobilla (*Cæsalpina brevifolia*), pomegranate rind (*Punica granatum*), and gall-nuts (*Quercus infectoria*), owe their tinctorial property to ellagic acid, and contain no member of the quercetin group. It is here pointed out that the plants examined hitherto contain, respectively, a tannin and colouring matter which yield on decomposition identical acids, and in some cases the same phenol.

106. "Ammonia and phenylhydrazine derivatives of $\alpha\beta$-dibenzoylcinnamene (anhydracetophenonebenzil)." By Francis R. Japp, F.R.S., and Alfred Tingle, B.Sc.

By oxidising dibenzoylcinnamenimide, $C_{22}H_{17}NO$—the first product of the action of ammonia on dibenzoylcinnamene—with chromium trioxide, the authors have obtained a mixture of *dibenzamide*, *benzamide*, and regenerated *dibenzoylcinnamene*.

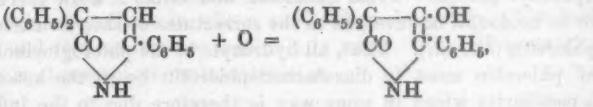
By reducing dibenzoylcinnamenimide with zinc dust and acetic acid in the cold, A. Smith's *triphenylpyrrhole*,  , melting at 140—141° (Trans., 1890, 57, 645), is formed.

The authors discuss the various reactions of dibenzoylcinnamene and dibenzoylcinnamenimide, and ascribe to these compounds the formulæ



It seems to be impossible to assign to dibenzoylcinnamenimide, for example, any other formula which will account for the formation of dibenzamide during oxidation.

By the oxidation of triphenylpyrrholone—the transformation product of dibenzoylcinnamenimide under the influence of heat—with chromium trioxide, the authors have obtained a compound which they regard as *triphenylhydroxypyrrholone* (m. p. 168°):



or one of its possible tautomeric forms. Heated with caustic potash, this compound evolves ammonia, and yields a mixture of benzilic and benzoic acids.

The authors have also studied the destructive distillation of the compound $C_{28}H_{22}N_2$ (m. p. about 230°), obtained by Japp and Huntly (Trans., 1888, 53, 184) by the action of phenylhydrazine on dibenzoylcinnamene. They find that it yields the 1:3:4-*triphenylpyrazole* obtained by A. Smith (*Annalen*, 1896, 289, 332) by the destructive distillation of tetraphenyldihydro-1:2-diazine. They point out that result renders it very improbable that the compound $C_{28}H_{22}N_2$ has the constitution of an anilidotriphenylpyrrhole, ascribed to it by Japp and Klingemann (Trans., 1890, 57, 671).

107. "Derivatives of cotoin and phloretin." By A. G. Perkin and H. W. Martin.

A study of the acetylisation of the diazobenzene derivatives of cotoin and phloretin.

Cotoin, $C_{14}H_{12}O_4$, a constituent of coto-bark, is, according to Ciamician and Silber, a monomethyl ether of benzoylphloroglucinol, $C_6H_2(OCH_3)(OH)_2{\cdot}CO{-}C_6H_5$ (*Ber.*, 1894, **27**, 409). *Cotoinazobenzene*, $C_{14}H_{11}O_4{\cdot}C_6H_5N_2$, forms orange-yellow needles, m. p. 183—184°. *Cotoin-azo-o-toluene*, $C_{14}H_{11}O_4{\cdot}CH_3{\cdot}C_6H_4N_2$, m. p. 203—204°, and *cotoin-azo-p-toluene*, m. p. 207—208°, crystallise similarly. *Diacetyl-azo-benzene cotoin*, $C_{14}H_9O_4(C_2H_3O)_2{\cdot}C_6H_5N_2$, crystallises in scarlet needles, m. p. 155—156°. As with the maclurin compound (Trans., 1897, **71**, 186), the acetyl-groups could be determined by Liebermann's method.

Phloretin, $C_{15}H_{14}O_5$, occurs in the root bark of the apple tree as a glucoside phloridzin. According to Ciamician and Silber, it has the constitution $C_6H_2(OH)_3{\cdot}CO{\cdot}CH(CH_3){\cdot}C_6H_4{\cdot}OH$. *Phloretin-disazobenzene*, $C_{15}H_{12}O_5(C_6H_5N_2)_2$, red needles, m. p. 254—256°, *phloretin-disazo-o-toluene*, m. p. 250—251°, and *phloretindisazo-p-toluene*, m. p. 250—251°, closely resemble the corresponding maclurin derivatives. *Acetyl phloretindisazobenzene*, $C_{15}H_{11}O_5(C_2H_3O)(C_6H_5N_2)$, forms orange-red needles melting at 217—219°. No higher acetyl derivative could be obtained. Comparing this result with those previously obtained with maclurin and phloroglucinoldisazobenzenes (Trans., 1897, **71**, 186), it would thus appear that phloretin contains only three hydroxyl groups. From Ciamician and Silber's work there appears to be no doubt, however, as to the correctness of their constitution for phloretin (*loc. cit.*). Thus, all hydroxyls in the phloroglucinol nucleus of phloretin must in diazobenzenephloretin be in the ketonic form, a peculiarity which in some way is therefore due to the influence of the phloretol group.

108. "Azobenzene derivatives of phloroglucinol." By A. G. Perkin.

Though phloroglucinol is known to yield azo- and disazo-derivatives as phloroglucinol-*p*-azobenzene sulphonic acid, $C_6H_5O_3{\cdot}N_2{\cdot}C_6H_4{\cdot}SO_3H$ (Stebbins, *Am. Chem. Soc. J.*, 1880, **2**, 240), and disazobenzenephloroglucinol, $C_6H_4O_3(N_2{\cdot}C_6H_5)_2$ (Weselsky and Benedikt, *Ber.*, 1879, **12**, 226), no trisazo-compounds have been previously obtained, though judging from its constitution the formation of such should be expected.

Phloroglucinoltrisazobenzene, $C_6H_3O_3(C_6H_5N_2)_3$, fine needles possessing a green iridescence which do not melt below 300°, is formed by addition of diazobenzene sulphate to a solution of phloroglucinol in aqueous sodium carbonate. Its production is independent of the amount of diazobenzene sulphate employed. It contains no free hydroxyl groups, being insoluble in alkaline solutions.

Phloroglucinol-o-trisazoanisol is prepared from phloroglucinol and *o*-diazoanisol in either sodium carbonate or acetate solution. No

corresponding disazo-compound could be obtained in this manner. It forms maroon coloured needles melting above 300°, insoluble in alkaline solutions.

Phloroglucinol-disazobenzene-m-azonitrobenzene, obtained from phloroglucinol-disazobenzene and *m*-diazonitrobenzene, forms dull red needles, m. p. 290°.

It is proposed to study the reaction of other substituted diazobenzenes with phloroglucinol under similar conditions.

109. "The action of phosphorus pentachloride on fenchone." By J. Addyman Gardner, M.A., and G. B. Cockburn, B.A.

Fenchone is acted on at the ordinary temperature very much more slowly than camphor, and the products of the action are different, for on pouring into water to get rid of the excess of phosphorus pentachloride and oxychloride, the authors obtained a crystalline compound of the formula $C_{10}H_{14}ClPO(OH)_2$, which they name chlorofenchone-phosphoric acid, and an oil consisting of unchanged fenchone and a substance containing chlorine, probably chlorofenchone.

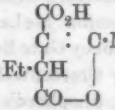
Chlorofenchone phosphonic acid is a white, crystalline solid, melting at 196°. It is very soluble in ether, alcohol, chloroform, and benzene, but more sparingly soluble in water. It is a dibasic acid, and the sodium salt crystallises in white, needle-shaped crystals. The lead, barium, and copper salts are insoluble in water. The oil containing chlorine is at present under investigation.

110. "Ketolactonic acid and its homologues." By C. H. G. Sprankling, B.Sc.,

In 1882, Young (Trans., 1883, **43**, 172) observed that when β-ethyl-acetosuccinic ether is slowly distilled, a little alcohol is liberated and on hydrolysis of the distillate with hydrochloric acid a crystalline acid, $C_8H_{10}O_4$, is formed in addition to α-ethyl-β-acetopropionic acid and a small quantity of ethylsuccinic acid.

The barium salt, $Ba(C_8H_9O_4)_2$, is obtained by the action of barium carbonate; a cold solution of barium hydrate gives the salt of β-ethyl-acetosuccinic acid, whilst at 100° barium carbonate is precipitated and the salt of α-ethyl-β-acetopropionic acid is formed.

From its composition, method of formation and behaviour it was concluded that the crystalline acid, to which the name ketolactonic acid was given, has the constitution



At Prof. Young's suggestion, these experiments have been repeated and a much larger yield of the crystalline acid has been obtained by prolonged heating of the β-ethylacetosuccinic ether before hydrolysis.

The lower homologues of the acid have also been prepared in a pure state from acetosuccinic ether and β-methylacetosuccinic ether respectively, and it has been found that by prolonged heating of β-isopropylacetosuccinic ether and subsequent hydrolysis with hydrochloric acid a very small quantity of the higher homologue is formed.

It is thus shown that the crystalline acid obtained by Young is the third member of a series to which the general name ketolactonic acid may conveniently be given. It will be necessary, however, to call the lowest member of the series ketolactonic acid, the others being named methyl, ethyl, isopropylketolactonic acid.

Ketolactonic acid, $C_6H_6O_4$ does not crystallise; methyl-ketolactonic acid, like the ethyl compound, forms colourless crystals, m. p. 176°.

The barium salts corresponding to those derived from the ethyl compound were prepared from ketolactonic acid and methyl-ketolactonic acid.

The rate of action of sodacetoacetic ether on the brominated fatty ethereal salts, the rate of elimination of ethyl alcohol from the β-alkylacetosuccinic ethers, and the rate of hydrolysis of the ethers differ greatly in the four cases examined, the rate in general diminishing rapidly with rise of molecular weight.

The hydrolysis of the β-alkylacetosuccinic ethers may take place in two ways—(*a*) the acetyl group is replaced by hydrogen and an alkylsuccinic acid is formed; (*b*) carbon dioxide is evolved and an α-alkyl-β-acetopropionic acid formed. With the ethers investigated, the higher the molecular weight of the alkyl group the larger is the relative yield of the alkyl succinic acid.

November 4th, 1897. Professor Dewar, F.R.S., President, in the Chair.

Messrs. Harold W. Harrie, W. R. Lang, W. H. Barlow, and A. V. C. Fenby were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Ernest George Annis, Health Office, Town Hall, Huddersfield; William Ball, 54, Stretton Road, Leicester; Richard Oxley Burland, J.P., Poolstock House, Wigan; Alexander McLean Cameron, Daylesford, Victoria; Owen Aly Clark, 12, Abbey Gate Street, Bury St. Edmunds; Alexander Clarkson, 2, Waveney Crescent, Ballymena, Ireland; Frank Collingridge, B.Sc., Kenmore, Shepherd's Hill, Highgate, N.; James Murray

Crofts, B.A., Richleigh, Gloucester; David Crole, Primrose Studios, Wellington Square, Chelsea, S.W.; John Daniell, Council of Education Laboratory, Johannesburg, S.A.R.; Andrew James Dixon, Dapto, N.S.W.; Robert Hamilton, 11, Ibrox Place, Glasgow; John Harger, B.Sc., Ph.D., The Nook, St. James's Mount, Liverpool; Charles Kelly, Oakmere, Hawarden, Cheshire; Tom Lemmey, B.A., Wellington College, Berks; James Scott Maclaurin, D.Sc., Mount Eden, Auckland, N.Z.; Allen Macmullen, 82, James Street, Dublin; Edward Masters, The Aloes, Hinckley Road, Leicester; John A. Mathews, 4, First Place, Brooklyn, N.Y.; Philip George Gregory Moon, 129, Rosary Road, Thorpe, Norwich; Joseph John Mooney, 34, Easter Road, Edinburgh; James Charles Philip, B.Sc., Ph.D., 16A, Merton Road, Victoria Road, Kensington, W.; Alexander Ferguson Reid, Stair Bridge, Stair, Ayrshire; Ernest Henry Roberts, Hollydale, Allfarthing Lane, Wandsworth, S.W.; Edward Sydney Simpson, 34, Pier Street, Perth, West Australia; Robert Francis Woodsmith, 89, Bartholomew Close, E.C.; Frederick William Steel, Tamunua, Navua River, Fiji; Michael Edmund Stephens, Avenue House, Finchley, N.; George Stubbs, Arnside, Hertford Road, East Finchley, N.; Edward Howard Tripp, Ph.D., Kent House, Blackheath Hill, S.E.; John Scriven Turner, 20, Bury Street, Bloomsbury, W.C.; Framjee Khurshedjee Viccajee, Hyderabad, Deccan, India; Percy John Vinter, Wesley College, Sheffield; Arthur James White, Whinsfield, Barrow-in-Furness.

Sir WILLIAM CROOKES then took the Chair, and of the following papers those marked * were read :—

***111. "On the properties of liquid fluorine." By Professors Moissan and Dewar.**

The nearest approach to the properties of the mythical alkahest or universal solvent of the alchemist is to be met with in fluorine. The transparent vessels in which it can be manipulated have to be made of some fluoride like fluor-spar, and such vessels are equally difficult to construct and ill-adapted for chemical manipulation. Modern research has, however, revealed the fact that the most powerful chemical affinities are completely suspended by allowing substances to come into contact at very low temperatures, and it appeared possible that even fluorine, which has the most powerful chemical activity of all the elements, might be manipulated in glass vessels under such conditions.

In a paper communicated to this Society entitled "The Liquefaction of Air and Research at Low Temperatures" (*Proc.*, 1895,

11, 221) speaking of fluorine, the author remarked, "This is the only widely-distributed element that has not been liquefied. Some years ago, Wallach and Hensler pointed out that an examination of the boiling points of substituted halogen organic compounds led to the conclusion that, although the atomic weight of fluorine is nineteen times that of hydrogen, yet it must in the free state approach hydrogen in volatility. This view is confirmed by the specific refractive index, which Gladstone showed was rather lower than hydrogen. If the chemical energy of fluorine at low temperatures is abolished like that of other active substances, then some kind of glass or other transparent material not so brittle as calcium fluoride could be employed in the form of a tube, and its liquefaction achieved by the use of hydrogen as a cooling agent."

The inference that fluorine approached hydrogen in volatility was deduced by Wallach and Hensler from a consideration of the boiling points of the fluorine derivatives of the benzene series.

The following table :—

I.

Benzene.	Boiling point.	Difference.	Toluene.	Boiling point.	Difference.
C_6H_6	80°	5°	$C_6H_5CH_3$	111°	5°
C_6H_5Fl	85°	47°	$p\text{-}C_6H_4Fl\cdot CH_3$	116°	44°
C_6H_5Cl	132°		$p\text{-}C_6H_4Cl\cdot CH_3$	160°	
Aniline.			**Benzene.**		
$C_6H_5NH_2$	183°	4°	C_6H_6	80°	8°
$p\text{-}C_6H_5Fl\cdot NH_2$ ..	187°	43°	$p\text{-}C_6H_4Fl_2$	88°	84°
$p\text{-}C_6H_4Cl\cdot NH_2$ ..	230°		$p\text{-}C_6H_4Cl_2$	172°	

shows that the substitution of 1 atom of hydrogen in these compounds by fluorine only causes an increase of the boiling point of from 4° to 5°, whereas chlorine causes an increase of from 45° to 50°. Such a relatively large ratio as 1 to 10 in the increment of boiling points suggests a great difference in the volatility of the elements fluorine and chlorine in the free state. A further examination of the properties of fluorine compounds, however, showed that the volatility of fluorine was not likely to approach that of hydrogen. This will be apparent from the following table :—

II.

Methane.	Boiling point (absolute).	Difference.	Ethane.	Boiling point (absolute).	Difference.
CH_4	110°	90°	C_2H_6.....	184°	58°
CH_3Fl	200°	50°	C_2H_5Fl...	242°	44°
CH_3Cl..... ..	250°		C_2H_5Cl...	286°	
CH_4	110°	149° = 4 × 37°	$C{\cdot}H_4$.....	110°	241° = 4 × 60°
CFl_4	259°		$C{\cdot}Cl_4$.....	351°	

Aldehyde.	B.p. (C.)		Benzaldehyde.	B.p. (C.)	
CH_3COH ...	21°	−11°	C_6H_5COH	179°	−18°
CH_3COFl ...	10°	41°	C_6H_5COFl	161°	38°
CH_3COCl ...	51°		C_6H_5COCl.	199°	

where it is seen that the substitution of hydrogen by fluorine in methane and ethane raises the boiling point by 90° and 60° respectively, and that the ratio of the increments of boiling point in corresponding fluorine and chlorine compounds is now not greater than 1 : 2. The boiling point of methyl fluoride was calculated from the critical point and vapour pressure of this substance as recorded by Professor Collie (Trans., 1889, **55**, 110). It will be noted as a curious fact that the substitution of fluorine in the aldehyde radicle causes a lowering of the boiling point and not an increase, and that the difference in boiling point between the chlorine and fluorine substitution body in either series is always between 40° and 50°. These considerations induced the hope that liquid air might give the command of a sufficiently low temperature for the liquefaction of fluorine, and that glass vessels might be used to collect the liquid. This view was supported by a consideration of the melting points of the halogens and the corresponding critical points deduced by following the suggestions of Clarke (*Am. Chem. Soc. J.*, 1896, **18**, 618), as to these relations. Thus the absolute melting points of chlorine, bromine, and iodine are respectively 171°, 267°, and 388°, and, assuming the same mean difference in melting point extended to fluorine, then its melting point would be 64° absolute. Now the critical points of chlorine and bromine are about $2\frac{1}{3}$ times the absolute melting points, thus giving 149° absolute, or −125°, as the probable critical point of fluorine. This critical value is only a few degrees lower than oxygen, and from this calculation the authors were entitled to assume that the position of fluorine as regards volatility would be somewhere between that of oxygen and nitrogen.

The following research was conducted in the Chemical Laboratory of the Royal Institution, to which Professor Moissan brought the apparatus for the production of gaseous fluorine with which his name will always be identified, and the authors had the invaluable assistance of Messrs. Lebeau, Lennox, and Heath in the conduct of the experiments.

Fluorine was prepared by the electrolysis of potassium fluoride in solution in anhydrous hydrofluoric acid. The fluorine gas was freed from vapours of hydrofluoric acid by being passed through a serpentine of platinum cooled by a mixture of solid carbonic acid and alcohol. Two platinum tubes filled with perfectly dry sodium fluoride completed the purification.

The apparatus used for liquefying the gas consisted of a small cylinder of thin glass, to the upper part of which was fused a platinum tube. This latter contained in its axis another smaller tube, likewise of platinum. The gas to be liquefied enters by the annular space, passes through the glass envelope, and escapes through the small inner tube. The glass envelope was fused to the platinum tube by which the fluorine was supplied.

The glass cylinder being cooled down to the temperature of boiling liquid oxygen ($-183°$), the current of fluorine gas passed through the bulb without becoming liquid. At this low temperature, however, the gas has lost its chemical activity, and no longer attacks the glass.

On lowering the temperature of the liquid oxygen by exhaustion, a yellow liquid is seen collecting in the glass envelope, while gas no longer escapes from the apparatus. At this moment the tube by which the gas had been escaping is stopped, so as to prevent air from entering and liquefying, and the glass bulb soon becomes full of a clear yellow liquid, possessed of great mobility. The colour of this liquid is the same as that of fluorine gas when examined in a stratum one metre thick. Fluorine thus becomes liquid, according to this experiment, at about $-185°$.

When the bulb containing the liquid fluorine is lifted above the surface of the liquid oxygen, the yellow liquid begins to boil with an abundant disengagement of gas, having all the energetic reactions of fluorine.

Silicon, boron, carbon, sulphur, phosphorus, and reduced iron, cooled in liquid oxygen and then placed in an atmosphere of fluorine, did not become incandescent. At this low temperature, fluorine did not displace iodine from iodides. However, its chemical energy is still sufficiently great to decompose benzene or oil of turpentine with incandescence. It would thus seem that the powerful affinity of fluorine for hydrogen is the last to disappear. The authors have noticed on some occasions that a current of fluorine gas passed into liquid oxygen gives a flocculent precipitate of a white colour, which quickly settles

to the bottom. If this mixture is shaken and thrown on a filter, the substance can be collected. It possesses the curious property of deflagrating with violence as soon as the temperature rises.

A new apparatus (Fig. 1) was constructed similar to that already described (that is to say, a glass bulb, E, fused to a platinum tube, A, which contained another similar smaller tube, D) but having each of the platinum tubes, B and C, fitted with a screw valve, in such a manner that at any moment communication—either with the outer air or with the current of fluorine—could be interrupted. This little apparatus was placed in a cylindrical glass vacuum vessel containing liquid oxygen, connected with a vacuum pump and manometer.

On repeating the former experiment with freshly prepared liquid air, instead of oxygen, fluorine easily becomes liquid at $-190°$ C. With liquid oxygen as refrigerant, the liquefaction of fluorine takes place at a temperature corresponding to the evaporation of the oxygen under a pressure of 437 mm. of mercury.

From these two experiments it results that the boiling point of fluorine is very close to $-187°$. This number is identical with Olszewski's boiling point of argon, so that this seems to be the first example of two gaseous elements boiling at the same temperature. It is a justifiable inference from the boiling point that the critical point must be about $-120°$, and thus, in all probability, the critical pressure is about 40 atmospheres, or less than half that of the critical pressure of chlorine, which is 84 atmospheres. This would make the critical constant for fluorine 4 as contrasted with chlorine, which has the value 5.

The following table gives the boiling points of the halogens:

	Absolute temperature.	Difference.
Fluorine.....	87°	
		153°
Chlorine.....	240°	
		97°
Bromine.....	337°	
		123°
Iodine	460°	

When the little glass bulb was three-quarters full of liquid fluorine, both the valves were closed, and then a good air pump caused the liquid oxygen serving as refrigerant to boil rapidly at a pressure of 2·5 cm. Under these conditions, a temperature of $-210°$ is reached, yet the fluorine did not show any sign of solidification, but retained its characteristic mobility. In future experiments it will be interesting to try the rapid ebullition of the liquid fluorine itself. During the

repetition of this experiment, a slight accident occurred. The screw of one of the valves becoming worn, allowed air to leak into the exhausted bulb. This air was immediately liquefied, and in a few moments two distinct layers of liquid were seen; the upper, colourless layer consisted of liquid air; the lower one, of a pale yellow colour, being fluorine.

To prevent the possible ingress of any air, the fluorine was introduced in its liquid state into a glass tube, the end of which was then sealed before the blow-pipe. The sealed tube, containing the liquid fluorine, was kept for a long time at $-210°$ by the rapid evaporation of a large quantity of liquid air, but it gave no trace of a solid body.

To determine the density of liquid fluorine, it was brought into contact with a number of bodies whose density is known, comparing their behaviour at the same time in liquid oxygen, which has about the same boiling point and density. By taking groups of bodies whose densities are very close to each other, it is easy to see which sink and which float in the liquid. This well-known though indirect method was the most suitable for these delicate experiments. The authors first satisfied themselves that the fluorine had no action on the materials used. To effect this, a crystal of ammonium thiocyanate (density = 1·31) was placed in a glass tube surrounded with boiling liquid air to the bottom of the tube, a current of fluorine gas was introduced by means of a platinum jet. The fluorine was rapidly liquefied, and the ammonium thiocyanate was not attacked. The same experiment was repeated with a fragment of ebonite ($d = 1·15$), of caoutchouc ($d = 0·99$), of wood ($d = 0·96$), of amber ($d = 1·11$), and of methyl oxalate ($d = 1·15$). It is of importance, in the experiments just mentioned, that the various materials used should be first kept at a temperature of $-190°$ for some little time before coming in contact with liquid fluorine.

In one of the experiments a piece of caoutchouc, having been insufficiently cooled, took fire on the surface of the liquid, and burnt completely away with a brilliant flame without leaving any residue of carbon. The piece of caoutchouc ran about the surface of the liquid like sodium on water, giving a very intense light.

The density experiment was carried out in the following manner:— In a glass tube closed at one end, and of which the lower part had been slightly drawn out, fragments of the five substances just mentioned were placed. The tube was then plunged to a third of its length into boiling liquid air. When it was all reduced to a temperature of about $-190°$ the fluorine gas was carefully introduced. This soon liquefied, and the wood and the caoutchouc floated easily on the surface of the pale yellow liquid. On the other hand, the methyl oxalate and ebonite remained at the bottom, while the amber

rose and fell in the liquid, appearing to be of the same density. The apparatus was shaken several times, and the quantity of liquid fluorine increased, but the results were the same.

The authors thus arrive at the conclusion from these experiments that the density of liquid fluorine is about 1·14. Another point which appears to be of interest is the following. The fragment of amber floating in the fluorine was very difficult to distinguish, which would seem to indicate that the index of refraction of liquid fluorine is in any case greater than that of liquid air or oxygen, although it is not likely to be so high as that of amber itself.

Fluorine was liquefied in a thick-walled glass tube which had been previously graduated, and the tube sealed. On cooling the tube and its contents to $-210°$, a contraction of $\frac{1}{14}$th in the volume of the liquid fluorine took place. A similar tube was left alone in a vacuum vessel full of liquid air. An hour and a half afterwards, the tube still being in liquid air, the fluorine had not changed in appearance. But shortly afterwards, when the air had all evaporated, a violent detonation occurred; the sealed tube and the double beaker in which it had been placed were smashed and reduced to powder.

Different samples of liquid fluorine examined with the spectroscope through a thickness of about $\frac{1}{2}$ cm. showed no specific absorption-bands in the visible spectrum.

Liquid fluorine placed between the poles of a powerful electro-magnet does not show any magnetic phenomena. These experiments are the more decisive, as comparative ones with liquid oxygen were made at the same time.

The capillary constant of fluorine is smaller than that of liquid oxygen. A capillary tube, plunged successively in fluorine, oxygen, alcohol, and water, gave the following figures:

Height of liquid fluorine	3·5	mm.
„ „ oxygen	5·0	„
„ alcohol	14·0	„
„ water	22·0	„

Liquid fluorine placed in a glass tube surrounded with liquid air (temperature about $-190°$ C.) had a slow current of hydrogen gas directed on to its surface by means of a fine platinum jet. There was immediate combustion with the production of flame. The experiment was repeated by dipping the platinum jet well below the surface of the liquid. At this temperature complete combination still took place, with a considerable evolution of light and heat.

Oil of turpentine, in the solid state, is attacked by liquid fluorine. To perform this experiment a little oil of turpentine was placed at the bottom of a glass tube surrounded with boiling liquid air. As soon as

a small quantity of fluorine was liquefied on the surface of the solid, combination took place with explosive force, a brilliant flash of light, and deposition of carbon. After each explosion, the current of fluorine gas was kept up slowly, a fresh quantity of liquid fluorine was formed, and the detonations succeeded each other at intervals of from 6—7 minutes. Finally, after a longer interval of about 9 minutes, the quantity of fluorine formed was sufficient to cause, at the moment of the reaction, the complete destruction of the apparatus. In several of these experiments a little liquid fluorine accidentally fell on the floor; the wood instantly took fire.

The action of liquid oxygen has been studied with more care, since the authors observed that by passing a current of fluorine through liquid oxygen, a detonating body could be produced.

If a current of fluorine is directed to the surface of liquid oxygen in a glass tube, the temperature being about $-190°$, the fluorine dissolves in all proportions, imparting a yellowish colour, and giving the liquid a graded tint from the upper to the lower part; the bottom of the tube is hardly coloured. If on the contrary, the fluorine gas is introduced at the bottom of the liquid oxygen, the yellow colour is produced at the bottom and diffuses slowly to the upper layers.

This phenomenon indicates that the densities of liquid fluorine and oxygen are very near each other. When the temperature of the mixture of liquid oxygen and fluorine is allowed to rise slowly, the oxygen evaporates first. The liquid becomes more and more concentrated as regards fluorine, and finally the latter begins to boil in its turn. In fact, at the commencement of this boiling the gas coming off will light a match which has only a red-hot point, and will not make lamp-black or silicon red-hot; but, on the other hand, the gas coming off at the end of the experiment will instantly cause these two latter bodies to burst into flame. When the glass bulb is completely empty and its temperature is rising, a distinct disengagement of heat is suddenly noticed, and the interior of the glass loses its polish. This rise in temperature is due to the fluorine gas attacking the glass. In this experiment, using perfectly dry oxygen, no precipitate is produced. If, on the contrary, oxygen is used which has been some hours in contact with the air, the detonating substance mentioned in previous experiments is produced.

The body which is produced by the action of fluorine on oxygen containing in suspension minute crystals of ice seems to be a hydrate of fluorine, decomposing, with detonation, by a simple rise of temperature. This view must, however, be taken as conjecture, until the real composition is ascertained. A small quantity of water at the bottom of a glass tube being cooled down to $-190°$, liquid fluorine formed on the surface of the ice as a mobile liquid without showing

any chemical action, and evaporated on the temperature rising. As soon as the apparatus became warmer the remaining gaseous fluorine attacked the ice with great energy, causing a strong smell of ozone.

A globule of mercury was treated in the same way as the water described above. The surface remaining very brilliant, the liquid fluorine surrounded it without causing any diminution of metallic lustre. On allowing the temperature to rise, the fluorine began to boil, and the liquid disappeared completely, without any attack of the mercury. The experiments seem to warrant the following conclusions.

Fluorine gas is easily liquefied at the temperature of boiling atmospheric air. The boiling point of liquid fluorine is $-187°$. It is soluble in all proportions in liquid oxygen and in liquid air. It does not solidify at $-210°$. Its density is 1·14, its capillarity is less than that of liquid oxygen; it has no absorption spectrum, and it is not magnetic.

Finally, at $-190°$ it has no action on dry oxygen, water, or mercury, but it reacts, with incandescence, on hydrogen and oil of turpentine. Future experiments must decide whether cooling below $-200°$ can suspend the powerful chemical action of liquid fluorine on hydrogen and hydrocarbons.

One of the most important questions for future investigation is the specific refractive and dispersive indices of the fluid. Davy, in his paper on the substances produced in different chemical processes on fluor-spar (*Phil. Trans.*, 1813, 278), says, "Dr. Wollaston has found that the fluoric combinations have very low powers of refracting light, and particularly the pure fluoric acid; so that the refracting powers of fluorine will probably be found lower than those of any other substance, and it appears to possess higher acidifying and saturating powers than either oxygen or chlorine."

Gladstone has shown that the specific atomic refraction of the combined element does not exceed 0·9, taking the Lorentz formula, and that the atomic dispersion diminishes instead of increasing for short wave-lengths. Further, he found that the other halogen substitution compounds gave atomic refractions nearly agreeing with the same substances in the free state. It has been found that liquid gases give the same atomic refraction as the gaseous body, so that the refractive index of liquid fluorine may be at once deduced provided it behaves like chlorine, bromine, or iodine. Taking 0·9 as the atomic refraction, the value would be, according to the Gladstone formula, 1·054, and the Lorentz, 1·081. Both values are far lower than those of liquid oxygen or air, 1·226 and 1·205 respectively. The general appearance of the liquid and the experiment with amber described above lead to the conclusion that liquid fluorine must have a refractive index much higher than that calculated. If the

refractive index is as great as 1·41, then the atomic refraction (Lorentz) will be 4·13, but if it is only about 1·192, then the atomic refraction will be 2. On both assumptions the atomic refraction of liquid fluorine is much greater than the value 0·9 found by Gladstone. Should the smaller value 2 turn out to be the correct one then the inference might be fairly drawn that the critical constant was also about 3, or nearly the value for oxygen. This view would make the critical pressure of fluorine about the same as that of oxygen, or 50 atmospheres. From this it would follow that, unlike chlorine, bromine, and iodine, which have the same atomic refraction in combination and in the free state, fluorine has a different value in the one state as compared to the other. In this respect it would appear to resemble oxygen, whose atomic refraction in combination may be only three-fourths of what it is in the free state. This view is confirmed by an examination of the atomic volume of fluorine. The other members of the halogen series have approximately the same atomic volume in combination as in the free state. Now, the atomic volume of fluorine in fluorbenzene is 11·5, or about half the atomic volume of chlorine, or taking chlorobenzene as standard, with chlorine as 22·7, then the atomic volume would be 10. The value for the free element appears to be 16·6, and the number deduced from liquid hydrofluoric acid about 15. Many metallic fluorides have relatively small atomic volumes. Thus the fluorides of cadmium, lithium, calcium, magnesium, and aluminium have an atomic volume just about half of that of the corresponding chloride. This difference is, however, easily explained if fluorine in the combined state has only half the atomic volume of chlorine. Dr. Thorpe's value for the atomic volume of fluorine, deduced from a study of the chloride and fluoride of arsenic, is 9·2, or free fluorine at its boiling point ought to have a density of 2, provided it behaved like the other halogens. This density for the free element is much too high, the experimental value being about 1·14. Such changes in atomic volume again suggest a resemblance with oxygen, and would lead to the inference that the refractive constants must also differ in the free and combined states. These interesting problems must, however, be left for future investigation.

Discussion.

Dr. Perkin said he felt much interested in the paper, because of the remarkable magnetic rotation of combined fluorine, for example, in fluortenzene. When one atom of hydrogen in benzene is displaced by chlorine, the rotation is considerably increased. The substitution of bromine causes a still higher rotation, and that of iodine the highest. On the other hand, the substitution of fluorine reduces the

magnetic rotation. He had suggested that this might be accounted for if fluorine were paramagnetic, because its magnetic rotation would then be the reverse of that of carbon and hydrogen. This, however, does not seem to be a probable explanation, since it is now found that liquid fluorine is not paramagnetic. It is possible that this element may have different values depending on whether it is free or combined. The nitro-group (NO_2) influences magnetic rotation much in the same way as fluorine.

Dr. GLADSTONE remarked on the importance of Professor Dewar's communication, the most interesting portion to him being that on the optical properties of the liquid fluorine. The specific refraction of that element had been calculated by him and his brother from fluorbenzene and from many salts, crystallised or in solution, with the invariable result that it was exceedingly small. In the last list of the specific refractions of the elements (*Proc. R. S.*, 1897, 60, 141) it is given at only 0·031, which is not a third of the next lowest in the list. Its specific dispersion is also low, and it has the additional peculiarity of giving a reversed spectrum. Now Prof. Dewar finds that liquid fluorine has about the same refractive index as that of amber; this is known to be 1·55 or thereabouts. As the specific gravity of the fluorine is stated to have been 1·14, we can easily calculate the specific refraction, viz., 0·482. This figure, instead of being the lowest in the list of elements, is nearly the highest, there being only six with higher values.

It is true that in some cases the specific refraction of an element in the free state differs somewhat from that deduced from its compounds. Fluorine would naturally be compared with the three halogens, chlorine, bromine, and iodine. Liquid chlorine has a specific refraction of about 0·27; in combination 0·28. Bromine has a specific refraction of about 0·20; in combination 0·21. Iodine vapour has a specific refraction of about 0·19; in combination 0·21. The free element, therefore, does not differ widely in specific refraction from the same element when in combination; and in each case is the smaller and not the greater of the two. A certain analogy does exist between fluorine and sulphur or phosphorus. These two when melted have high specific refractions, sulphur being 0·50, and phosphorus 0·59; these high figures are generally much reduced when the elements are in combination, but the extent of this reduction is by no means comparable with what would appear to be the case with fluorine. Although Professor Dewar's method is correct in principle, Dr. Gladstone expressed a strong hope that accurate determinations would be made by one or other of the more direct methods.

Dr. THORPE said, in reference to the allusion by the President to his determination of the specific molecular volume of fluorine as far back

as 1880, that too much stress could not be laid upon the particular value viz., 9·2, which he then obtained. It was deduced from a study of the specific gravity and thermal expansion of arsenic fluoride, a substance which is not easy to obtain pure, and which is not altogether without action on glass, especially at temperatures approaching the boiling point. It, moreover, presupposes that arsenic fluoride has a molecular constituent analogous to that of arsenic chloride. Such an assumption is probable, but having regard to the remarkable complexity of many fluorine compounds, as, for example, hydrogen fluoride itself, when compared with the corresponding chlorine compounds, the supposition cannot, at present, be regarded as more than probable. The particular value obtained, however, clearly indicated the order of the magnitude, as shown by its substantial agreement with the other values quoted by the author.

With respect to the question raised by Dr. Gladstone, he might say that the peculiar behaviour of glass when immersed in arsenic fluoride was significant, and suggested a method by which the refractivity of liquid fluorine in the free state might be ascertained with a fair approximation to accuracy, viz., on the same principle as that adopted by the authors in determining the relative density of liquid fluorine—that is, by immersing solids of known refractivity in the liquid, and observing which became invisible. Arsenic fluoride is a highly refractive liquid, and some specimens of glass threads and tubes become almost invisible when immersed in it.

Professor DEWAR, in reply, observed that he did not intend to convey the impression that, because amber in liquid fluorine might be difficult to define clearly, it necessarily followed that the refractive index would turn out to reach 1·55, as Dr. Gladstone seemed to infer. His present impression was that it exceeded that of liquid air, but he could go no further. No doubt the next time Professor Moissan and he had the opportunity of continuing the experiment, a direct determination of the refractive index would be made.

*112. "The liquefaction of air and the detection of impurities." By Professor Dewar.

In a paper on "The relative behaviour of chemically prepared, and of atmospheric nitrogen," read before the Society in the year 1894, it was stated that all samples of nitrogen and oxygen properly purified, are, when liquefied, clear transparent liquids, so that the solid matter which always separates when air or nitrogen or oxygen is liquefied on the large scale consists of impurities. Ordinary air, containing 4 parts of carbonic acid per 10,000 parts gave a turbid liquid from the solidification of the carbonic acid; and oxygen containing traces of

Apparatus for Liquefaction of Fluorine.

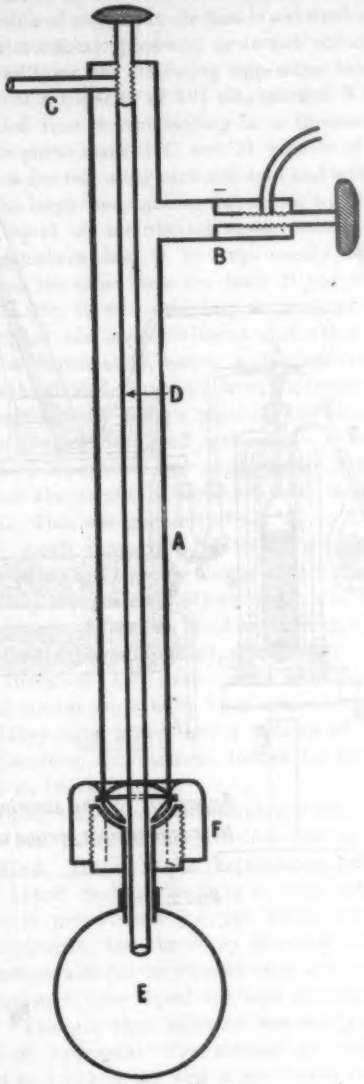


Fig. 1.

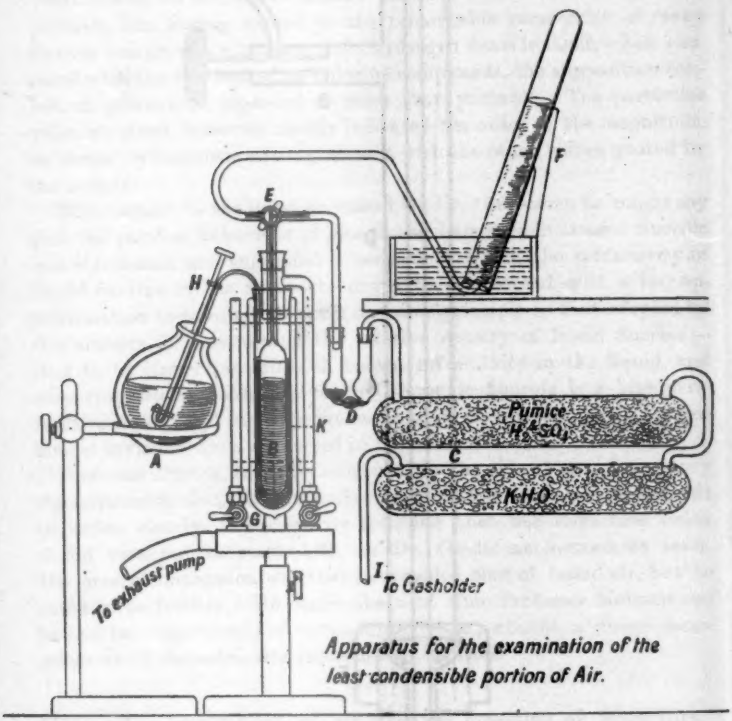

F
E
H
K
D
A
G
C
Pumice
H_2SO_4
KHO
To exhaust pump
I
To Gasholder
Apparatus for the examination of the least condensible portion of Air.

FIG. 2.

chlorine behaved in a similar manner. With the object of ascertaining the proportion of any gas in air that is not condensable at about −210° C. under atmospheric pressure, or is not soluble in liquid air under the same conditions, the following apparatus has been devised. A cylindrical bulb of a capacity of 101 c.c., marked B in figure, had a capillary tube sealed into it terminating in a three-way stopcock, as shown at E. The parts marked C and D consist of soda-lime and sulphuric acid tubes for removing carbonic acid and water. The stand marked G holds the large vacuum test tube into which B is inserted which holds the liquid air maintained under continuous exhaustion. As this low temperature had to be kept steady for from one to two hours, while at the same time the bulb B had to be completely covered with liquid air, it was necessary to arrange some means of keeping up the liquid air supply without disturbing the apparatus. The plan adopted is shown at H, which is a valve arrangement which can be so regulated as to suck liquid air from the large vacuum vessel A and discharge it continuously along a pipe into the vacuum test tube G, the latter being kept under good exhaustion. In working the apparatus, the tube I is connected to a gasometer containing 10 cubic feet of air, so that the volume of air condensed in each experiment may be observed. This was generally from 2½ to 3 cubic feet. If there is a very small proportion of some substance not liquefiable or soluble in liquid air, then we should expect the vessel B would not fill up completely into the capillary tube. This is, however, exactly what does take place. After 40 minutes' cooling, the vessel B and the cool part of the tube were filled with liquid. In this experiment some 80 litres of air were condensed, and any accumulated uncondensed matter must have been concentrated in the upper part of the capillary tube which had a volume of 0·5 c.c. Under the conditions, therefore, the material looked for must be less than 1 part by volume in 180,000 of air.

To test the working with an uncondensable gas added to air, a volume of 10 cubic feet was taken in the gasholder and to that 500 c.c. of hydrogen were added. This is in the proportion of less than 1 in 500. Even after two hours' cooling, the tube B could only be filled four-fifths. In order to prove that the gas accumulated in the upper part of B was hydrogen, the three-way stopcock at E was turned, and the temperature allowed to rise so that the gas was expelled from the evaporation of the liquid air and collected over mercury as shown at F. The gas thus collected was easily combustible and consisted chiefly of hydrogen. The amount of hydrogen was then reduced to 1 part in 1,000 of air, and it was found that after one and a quarter hour's cooling the bulb B had filled to within a half c.c. of the capillary tube. A new sample of air containing 1 part of hydro-

gen in 10,000 of air filled the bulb B completely as if it were ordinary air.

It appears from these experiments that 1 part of hydrogen in 1,000 of air is just detectable by this plan of working. As the 80 litres of air condensed contained some 80 c.c. of hydrogen, it appears that 100 c.c. of liquid air at from $-200°$ to $-210°$ C. had dissolved nearly all this gas; in fact, that 20 c.c. of hydrogen at the low temperature is dissolved in 100 c.c. of liquid air. In the paper on "The liquefaction of air and research at low temperatures" (Proc., 1895, 11, 221), it was shown that if hydrogen containing a small percentage of oxygen were employed for the purpose of getting a hydrogen jet, the liquid collected from it was oxygen, containing, however, so much hydrogen dissolved in it that the gas coming off for a time was explosive.

In order to press this inquiry a little further, some natural gas known to contain a different constituent like helium suggested itself as being worthy of trial. Lord Rayleigh's results of the examination of the gas from the King's Well at Bath showed that it contained 1·2 part of helium per 1,000 volumes, so that it seemed admirably adapted for such experiments. The author has to express his thanks to the Corporation of Bath for giving permission to collect samples of the gas.

The sample of gas from the Bath Spring was treated exactly in the same way as the hydrogen mixtures described above. During the liquefaction there was a marked difference in the appearance of the liquefied gas, for while the hydrogen and air mixtures gave a clear, transparent liquid, the product from the Bath gas was turbid, and the precipitate by transmitted light looked yellow-brown. This solid turns out to be of organic origin, probably of the petroleum order of compounds. It has a very marked aromatic smell resembling such bodies. The trace of material left, gave, after treatment with concentrated nitric acid, the smell of nitrobenzene; and as its detection cannot be explained by the presence of any material of the kind in the vessels used in collecting, it must be assumed to be a normal constituent of the Bath gas. A further quantity of the Bath gas must be collected in order to confirm the presence of such bodies and to definitely make out their nature. Another peculiarity of the liquid is that, on examining it with the spectroscope, even through a thickness of 2 inches, no trace of the characteristic oxygen absorption spectrum could be detected. In all attempts to make nitrogen for liquefaction on the large scale, oxygen could always be detected in the liquid with the greatest ease by means of its absorption spectrum. After the cooling had continued for 1 hour the gas ceased to flow into the condensing vessel, and some 20 c.c. at the upper part of the glass cylinder B was filled with a gas that had not undergone liquefaction or solution. About 70 litres of the Bath gas were condensed, certainly the largest

quantity of this gas ever subjected to chemical examination. This was boiled off just as the hydrogen was treated in the experiments described above, and as, by accident, too much nitrogen had volatilised along with the gas, oxygen was added and the mixture sparked over alkali to get rid of the excess of nitrogen. During the sparking, the helium lines were well marked (along with others the origin of which must be settled later), and a vacuum tube filled with the product of the sparking gave a splendid spectrum of the gas. The sample of gas directly collected from the liquid nitrogen contained about 50 per cent. of helium. It is therefore possible to separate helium from a gas when it is only present to the extent of one-thousandth part by liquefaction in the manner described. From this it would appear that helium is less soluble in liquid nitrogen than hydrogen is in liquid air, and is of greater volatility than either of the constituents of air, as Professor Olszewski found (*Bull. Ac. Crac.*, 1896, 297) by direct experiment on a pure sample of the gas sent to Cracow by Professor Ramsay with the object of liquefaction. In the author's lecture (*Proc. Roy. Inst.*, 1896), entitled "New researches on liquid air," the following observation occurs: "The exceptionally small refractive value observed by Lord Rayleigh in the case of helium shows that the critical pressure of this body is proportionately high. It would therefore be more difficult to liquefy than a substance having about the same critical temperature but possessing a lower critical pressure than hydrogen." Now that it has been shown by Professor Moissan and the author that two substances like fluorine and argon, differing by 2 units in molecular weight, boil at nearly the same temperature, it seems reasonable to extend the analogy to the case of hydrogen and helium where the same difference occurs, and to suggest that they also probably have about the same volatility. If the sample of uncondensed gas resulting from the first liquefaction of the Bath gas were again treated in the same way, a much more concentrated specimen of helium could be obtained. Provided helium were wanted on a large scale, then a liquid air apparatus similar to that in use at the Royal Institution transported to Bath and worked with the gas from the King's Well could be made to yield a good supply. With a modified form of apparatus, it will be possible to collect any residuary gas from the use, not of 3 cubic feet of air or Bath gas, but from hundreds of cubic feet of such products. This investigation will be continued with new samples, in order to see if the composition of the gases changes and to isolate the hydrocarbons.

The author has to thank Mr. Lennox and Mr. Heath for able assistance in carrying out the experiments.

Discussion.

Sir William Crookes said that a few days ago he received from Professor Dewar a tube containing some of the gas at atmospheric pressure. A small quantity was let into a new and completely exhausted spectrum tube, which was then re-exhausted and filled several times. On exhausting to 5 mm. pressure and passing an induction spark it showed the nitrogen spectrum brilliantly, and on intercalating a condenser the yellow helium line was visible, but too faint to be measureable in the large spectroscope. To remove the nitrogen, 47 c.c. were mixed in an eudiometer with an equal volume of oxygen, and sparked for about 8 hours, absorption of the products being effected by strong potash solution over the mercury. When contraction had ceased, the residual oxygen was absorbed by passing pyrogallol into the potash. The unabsorbed gas amounted to 25 c.c. This gas, dried over phosphoric anhydride, was examined in a new spectrum tube, end on. (Tube shown in action.) It gave the helium line (wave-length 5875·87) brilliantly, together with the other helium lines. No argon lines could be seen.

*113. "The absorption of hydrogen by palladium at high temperatures and pressures." By Professor Dewar.

One of the author's earliest papers was entitled "The motion of a palladium plate during the formation of Graham's hydrogenium." The explanation of the motion together with a record of other experiments can be found in the *Proc. Roy. Soc. Edin.*, 1868, **6**, 504.

A subsequent investigation by the author into the physical constants of hydrogenium appeared in the *Trans. Roy. Soc. Edin.*, 1876, **27**, 167, and had reference to the specific gravity, specific heat, and coefficient of expansion of the occluded hydrogen. These observations led to the conclusion that the specific gravity was independent of the amount of condensed gas, and had a mean value of 0·62. The specific heat, relatively to palladium, of the condensed hydrogen appeared to vary inversely as the quantity occluded, but taken relatively to successive charges was nearly constant, having the value 3·4, which is identical with that of gaseous hydrogen at constant pressure. The coefficient of cubical expansion of the alloy is about twice that of palladium, and that of the hydrogen in its compressed state not more than three times that of mercury. A later communication was made to the Philosophical Society of Cambridge (*Proc.*, 1878, **3**, 207) dealing with the thermo electric relations and electric conductivity of hydrogenium. It was shown that the potential difference of a junction of hydrogenium-

palladium is at ordinary temperature nearly equal to that of an iron-copper junction, and that it increases with the temperature according to the general parabolic law; the rate of the increase being, however, greater than iron-copper and subject to a regular variation on account of successive heatings. The formation of thermo-electric piles, and of neutral points in a wire of this substance, along with the continuous formation of thermo-electric currents through the application of a hydrogen flame were explained. Experiments on electric resistance proved that it increases directly with the amount of hydrogen condensed in the palladium.

Subsequent investigators have dealt more elaborately with the many problems suggested by hydrogenised palladium, but so far the essential facts referred to above have been confirmed.

In the course of the early observations the following experiment is recorded as illustrating the absorption of hydrogen by palladium at a red heat.

Take a strip of thin sheet palladium, 4 or 5 cm. long, and about 5 mm. in breadth, clamp it firmly by the end in a suitable support, so that the strip is free to vibrate, and insert it edgeways in the middle of a hydrogen flame, burning from a nozzle about 1 mm. in diameter. If the palladium be now depressed into the inner dark cone it immediately begins to vibrate, producing a low, musical note.

If the flame be extinguished by stopping the current of hydrogen for an instant, on allowing the gas to flow, the vibration commences again, and may be kept up without any actual flame.

The motion in this position in the flame is due to the absorption of hydrogen on the cool side next the inner cone, with its attendant increase of length, producing a bending of the sheet into the hot portion of the flame, where the hydrogen is instantly expelled from the palladium, which is forced to return to its original position from its natural elasticity.

It is now known that no absorption of hydrogen at atmospheric pressure by palladium takes place above 145° C., so that the cause of motion must originate at a comparatively low temperature. The question arises, Can palladium, under any condition of pressure, absorb hydrogen at a red heat in quantity at all comparable to what it can do at lower temperatures? If free hydrogen and palladium-hydrogen are compared as regards volatility, the one boils at 30° (abs.), the other at 420° (abs.), very much like two isomeric forms of the same substance. This ratio of 1 : 14 given (and certainly the ratio could not be made greater than 1 : 16, since the absolute boiling points may be taken as in the ratio of their respective critical points) we thus arrive at a hypothetical palladium-hydrogen critical point of 640° (abs.) or 366° C. An almost exact parallel may be drawn between

palladium-hydrogen in its relation to free hydrogen and iridium oxide in its relation to free oxygen. Thus liquid oxygen boils at 90° (abs.) and the tension of dissociation of iridium oxide is 1 atmosphere at 1423° (abs.). The ratio of the absolute boiling points of liquid oxygen and the oxygen of iridium oxide are therefore as 1 : 15·9, which is almost the same value as that found above for the relative volatilities of hydrogen and palladium. In either case, the ratio of the absolute boiling points of the respective substances may be taken as approximately representing the ratio of the latent heats of transition of state. It might then be possible that palladium no longer absorbed hydrogen under any condition of pressure. The present experiments were undertaken with the view of answering this question.

The diagram (3) shows the general arrangement of the apparatus most suitable for examining the behaviour of the metals like palladium, sodium, potassium, &c., towards hydrogen at high temperatures and pressures.

A rod of palladium A weighing about 119 gms., kindly placed at my disposal by Mr. George Matthey, F.R.S., was placed in a strong steel cylinder D having an accurately fitting conical joint. As little extra space as possible was left in the cylinder, which was heated in a bath of fusible metal E. The vessel was connected with the manometer B by a strong copper tube, and the latter was similarly joined to a compressed gas cylinder H containing hydrogen. The apparatus, without the palladium, must be carefully tested at high pressures and temperatures. There must be no trace of a leak. An extra stopcock at C enabled the hydrogen accumulated in the apparatus to be blown off suddenly when required, after the hydrogen cylinder stopcock was shut off. Before commencing the experiments at high temperatures, it is well to charge the apparatus to a pressure of 20 atmospheres with hydrogen and then blow off the gas and measure it. In this way the volume of hydrogen that is absorbed for every diminution of the pressure of hydrogen is known. In the first experiments a pressure of 20 atmospheres of hydrogen in the apparatus corresponded to 780 c.c. of gas, measured at atmospheric pressure. When the fusible metal bath was heated to 420° and hydrogen at a pressure of 80 atmospheres introduced at starting, it fell to a pressure of 60 atmospheres in $2\frac{1}{2}$ minutes. Blowing off the gas instantly to get rid of accumulated impurities and again applying a pressure of 80 atmospheres of hydrogen, the pressure was reduced to 60 atmospheres in 6 minutes. When the same operations were repeated a third time, the diminution of pressure by 20 atmospheres took 16 minutes, and a fourth operation required 28 minutes. In all, therefore, upwards of 3,000 c.c. of hydrogen were absorbed in less than an hour. If the palladium could

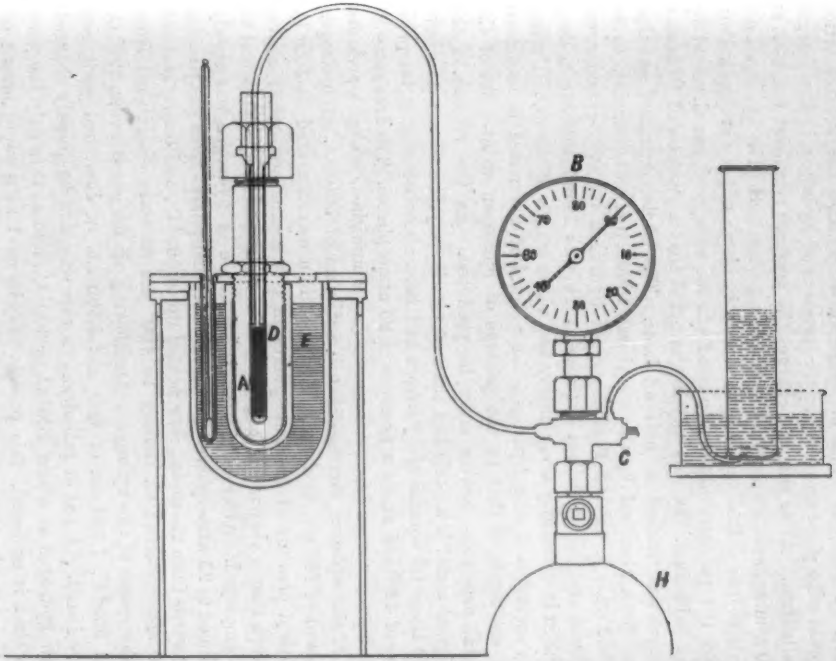


FIG. 3.

be seen at about a low red heat, then during the rapid absorption of the hydrogen as described in the last experiment, the temperature must rise very considerably, and the metal, during the operation, must actually appear to grow much brighter. Calculating from the tensions of the gas, the evolution of heat at 300° must be about 4698 gram-units of heat per gram of hydrogen absorbed. The reverse action would take place on reducing the pressure of hydrogen in the charged palladium. After the four charges the pressure remained constant at 80 atmospheres, no more hydrogen being absorbed. The hydrogen gas outside the palladium was now suddenly blown off, the stopcock shut, and the pressure allowed to rise from the escape of gas absorbed by the palladium. In this way it was noted that a pressure of 40 atmospheres was reached in half an hour. The whole amount of gas that had been absorbed by the metal was found, on measurement, to be 2,980 c.c. After the first charge of hydrogen the steel cylinder was opened and the palladium examined. It was found to have a deep rent in it extending along nearly the whole length of the rod. During the occlusion of the hydrogen the volume of the metal is increased by one-tenth, so that in the passage of hydrogen in and out of the metal enormous strains must be produced. As the volume of the original metal is a little less than 10 c.c., it may be taken that above 300 times its volume of hydrogen had been absorbed at the temperature of 420° and under a pressure of 80 atmospheres. The free space in the manometer and connections was now diminished, so that a pressure of 20 atmospheres corresponded to a volume of 300 c.c. of hydrogen instead of 780 c.c. as above. The palladium was saturated at 360° C. under a pressure of 80 atmospheres in the manner described above, except that a very much larger number of charges of hydrogen had to be employed. After saturation, the pressure of hydrogen was slowly reduced to 25 atmospheres: it rose to 30 atmospheres from gas passing outwards from the metal, now heated up to 500° C., and finally reached 100 atmospheres; on cooling to 400° the pressure diminished from reabsorption of the hydrogen. On blowing off the gas between 400° C. and 500° C. 1,400 c.c. of free and 3,300 c.c. of combined hydrogen were found. A rod of palladium, in this way, can be quickly charged with hydrogen at about 300° C. or 400° C., and as it is only the pure gas that is occluded, this process may be used as a rapid means of getting pure hydrogen in quantity for experimental purposes.

In the next experiment, the palladium was heated to 500° C. before any hydrogen under pressure was applied. No absorption was observed till the pressure of hydrogen reached 60 atmospheres. On charging as before at pressures between 80 atmospheres and 60 atmospheres, the metal was found to absorb 1,900 c.c. of gas. The experiment was repeated, with the difference that the charging pressure of hydrogen

was raised to between 120 atmospheres and 100 atmospheres, and it was found that the palladium had now occluded 3,700 c.c. of hydrogen. Thus it appears from these experiments that at 500° C. palladium can still occlude 300 times its volume of hydrogen under a pressure of 120 atmospheres. The observations on the tension of hydrogen in palladium by Troost and Hautefeuille showed that, for the same temperature, the values became constant and independent of the amount of occluded gas, only when the volume of hydrogen absorbed lay between 200 and 600 times that of the metal. Any other proportions gave variable tensions for the same temperature. The fact that 300 volumes can still be occluded at 500° C. seems to show that palladium and hydrogen, under such conditions, still follow the same laws of absorption as at lower temperatures. Nothing analogous to a critical point, where no combination takes place between the metal and hydrogen, has been reached.

Hoitsema published an important paper on palladium-hydrogen tensions in the *Archives Neerlandaises*, 1896, **30**, 44. In this memoir, Hoitsema gives also a series of observations on the same subject made by Roozeboom. Taking the tensions given by the latter (simply because the curve seems more regular) for the horizontal portions of the dissociation curves at different temperatures, and calculating a Willard Gibbs' formula, from the following data, viz., 20° C. pressure 7 mm.; 100° C. pressure 205 mm.; 170° C. pressure 1467 mm., the expression results (where T is the absolute temperature)

$$\log. p = 7{\cdot}00338 - \frac{1983{\cdot}4}{T} + 0{\cdot}2378 \log. T.$$

From this it follows that the latent heat of dissociation of the palladium-hydrogen per atom of hydrogen in gram-units is $4561 + 0{\cdot}2378\,T$. This would seem to show the latent heat of dissociation increases instead of diminishing with temperature. In other words, the heat of combination should be rather greater at higher temperatures, instead of diminishing as it must do if a point where no occlusion takes place were being approached. Thus theory and experiment would seem to agree.

The best and safest method for the experimental study of the relations of hydrogen and palladium at high temperatures and pressures would be to investigate the change of electrical resistance in a heated wire of the metal when subjected to different hydrogen pressures. The problem is, no doubt, more complicated, still interesting results must follow from such an investigation. Some of the electrical properties of hydrogen and palladium at low temperatures have been determined by Professor Fleming and the author, and the results will appear in future publications bearing on the subject.

The author is indebted to Mr. Robert Lennox for able assistance in the conduct of the experiments.

Discussion.

Mr. R. J. Friswell asked whether the President had made any measurements of the tensile strength of the steel. He was astonished to hear of the metal standing 100 atmospheres at over 500° C. He was asking for information, as he had been unable to obtain any data as to the strength of metals near a red heat, a point at which it must be rapidly falling away. The matter was of great interest for experimenters using autoclaves. Engineers did not seem to have done any work on tensile strength at points above the temperatures usual in steam boilers.

Prof. Dewar, in reply to Mr. Friswell, agreed that no engineering formulæ existed. The experiments were dangerous, but one had to take the risk. The metal used was Whitworth compressed steel, and the vessel was made by drilling out a solid mass. He had no data as to tensile strength, the results were desired and the risk taken.

114. "On some yellow vegetable colouring matters." By A. G. Perkin.

The *Rhus rhodanthema*, a tree growing to the height of 70 or 80 feet, is indigenous to northern New South Wales. The colouring matter $C_{15}H_{10}O_6$ is indentical with fisetin. A *glucoside* of fisetin, $C_{36}H_{30}O_{16}$ (C = 60·18 ; H = 4·45), colourless needles, m. p. 215—217°, is also present ; it is decomposed with difficulty by boiling dilute acids. This closely resembles fustin, $C_{58}H_{46}O_{23}$ or $C_{36}H_{26}O_{14}$ (C = 63·34 ; H = 3·81), m. p. 217—219°, the fisetin glucoside of *R. Cotinus* (Schmid, *Ber.*, 1886, 19, 1753), but differs from it in percentage composition. Its decomposition with acid would be closely expressed by the equation $C_{36}H_{30}O_{16} + 2H_2O = 2C_{15}H_{10}O_6 + C_6H_{14}O_6$, if rhamnose or glucose are liberated by this reaction. Gallic acid was also isolated, evidently as a decomposition product of gallotannic acid contained in the wood.

Berberis ortuensis, a plant resembling *Berberis vulgaris*, flourishes in Cyprus. It was found to contain berberine, but no colouring matter of the mordant yellow class.

The perianths surrounding the seeds of *Rumex obtusifolius* contain a trace of quercetin, which is interesting, as in many roots of this species methylanthraquinone derivatives also exist. It is also pointed out that the leaves and green stems of madder (*Rubia tinctoria*) contain a yellow colouring matter which will be examined.

115. "Naphthylureas." By George Young, Ph.D., and Ernest Clark.

The mononaphthylureas may be prepared by the action of potassium cyanate on the hydrochloride of the corresponding naphthylamine. In consequence of the rapid conversion of the mononaphthylureas into the symmetrical di-naphthylureas which takes place on heating, even below the melting points of the former, the true melting points have escaped the observation of previous authors. α-Naphthylurea melts at 213—214°, at which temperature it is converted into di-α-naphthylurea, melting at 284—286°. β-Naphthylurea melts at 213—215°, and immediately forms di-β-naphthylurea, melting at 289—290°. Acetyl-α-naphthylurea, m. p. 214—215°; benzoyl-α-naphthylurea, m. p. 243—243·5°; acetyl-β-naphthylurea, m. p. 202—203·5°; benzoyl-β-naphthylurea, m. p. 219—220°.

116 "Benzoylphenylsemicarbazide." Preliminary notice. By George Young, Ph.D., and Henry Annable.

In a previous communication presented to the Society (Trans., 1897, 71, 200), attention was drawn to the disagreement between the melting points of benzoylphenylsemicarbazide, 202—203°, as observed by Michaelis and Schmidt (*Ber.*, 1887, **20**, 1713), and 210—211° as observed by Widman (*Ber.*, 1893, **26**, 945). It described the preparation and examination of this substance—melting at 202—203°—and suggested the possible existence of two benzoylphenylsemicarbazides both having the constitutional formula, $C_6H_5N(COC_6H_5)\cdot NH\cdot CO\cdot NH_2$. Shortly after the publication of this paper, Dr. Widman had the courtesy to submit a sample of his preparation for comparison. This sample had been observed by Dr. Widman to melt at 210—212°; the authors found it to melt at 211—212°. Their thermometer agreed therefore with Dr. Widman's. A comparison of the properties of the two preparations led to exceedingly interesting results. Widman's benzoylphenylsemicarbazide seemed to be almost, if not quite, insoluble in boiling benzene, the melting point remaining unaffected. The authors' benzoylphenylsemicarbazide was fairly soluble in boiling benzene, crystallising out again on cooling. Mere recrystallisation from benzene did not affect the substance, but prolonged boiling with benzene caused a gradual rise of the melting point. On the other hand, the substance was easily soluble in boiling water and crystallised out on cooling unchanged, whereas Dr. Widman's preparation dissolved in boiling water with difficulty and crystallised out on cooling, with the melting point considerably lowered. These results induced the authors to undertake a thorough investigation of the formation and properties of benzoylphenylsemicarbazide. They have

been able to determine that the action of benzoyl chloride on phenylsemicarbazide produces under different conditions three distinct forms of benzoylphenylsemicarbazide. These three forms melt respectively at 202—203°, 205—206° and 210—211°. They are each capable of conversion into either of the other two. They exhibit different and characteristic crystalline structures under the microscope. They possess different solubilities and densities. The form of highest melting point seems incapable of solution without undergoing at least partial change into one or other of the lower melting forms, but pure solutions of these latter may be easily prepared. These solutions have no action on polarised light. The authors are at present engaged in examining the physical properties of these substances and in extending the investigation to a number of other closely related compounds, in the hope of being able to determine whether they are capable of existence in two or more modifications.

117. "Sulphocamphylic acid." By W. H. Perkin, jun.

In a previous communication (Proc., 1895, 11, 23) it was shown that when the potassium salt of sulphocamphylic acid is treated with phosphorus pentabromide, the sulphobromide, $C_8H_{12}(SO_2Br)\cdot CO_2H$, is produced, and from this substance by elimination of sulphur dioxide an acid of the formula $C_8H_{12}Br\cdot CO_2H$ was obtained, which, as it gives β-camphylic acid, $C_8H_{11}CO_2H$, on treatment with alcoholic potash, may be called *bromodihydro-β-camphylic acid.*

During the course of further experiments, the corresponding *camphylic sulphochloride*, $C_8H_{12}(SO_2Cl)CO_2H$, has been obtained by treating the potassium salt of sulphocamphylic acid at 0° with phosphorus pentachloride. This substance melts at 168—170°, and at the same time slowly undergoes decomposition with evolution of sulphur dioxide and formation of *chlordihydro-β-camphylic acid*, a crystalline substance which melts at 105—106°.

Like the corresponding bromo-compound, it is decomposed by boiling with alcoholic potash, with elimination of hydrogen chloride and formation of β-camphylic acid.

In the last communication on sulphocamphylic acid (Proc., 1896, 12, 189) it was stated that, when β-camphylic acid was treated with phosphorus trichloride, and the product distilled under reduced pressure, the chloride of an acid melting at 130° is obtained which was called iso-β-camphylic acid, because at the time it was thought that this acid might prove to be isomeric with β-camphylic acid. It has since been found that the reaction does not proceed in this way, but that the following much more remarkable change takes place. When the chloride of β-camphylic acid is distilled, there is, as already men-

tioned, some decomposition and charring, and during this distillation the chloride is *reduced* almost completely to the chloride of an acid, $C_9H_{14}O_2$, which on investigation has been found to be identical with isolauronolic acid, the acid which Koenigs and Hoerlin (*Ber.*, 1893, **26**, 813), and the author (Proc., 1893, **9**, 109) obtained by the elimination of sulphuric acid from sulphocamphylic acid.

This same isolauronolic acid (together with a liquid acid, which is possibly an isomeride) is obtained when β-camphylic acid is reduced with sodium amalgam under certain conditions, and quite lately it has also been obtained in large quantity by fusing sulphocamphylic acid with soda in a cast-iron pot.

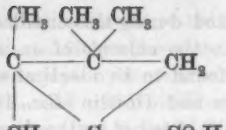
When fused in a nickel dish with caustic soda, sulphocamphylic acid yields a mixture of α- and β-camphylic acids, $C_9H_{12}O_2$, but when an iron pot is used, the iron acts as a reducing agent, and the product, which is found to contain quantities of ferric oxide, on treatment in the usual way yields large quantities of isolauronolic acid, $C_9H_{14}O_2$.

Isolauronolic acid is, as Koenigs and Meyer (*Ber.*, 1894, **27**, 3466) showed, readily oxidised to isolauronic acid, $C_9H_{12}O_3$, a ketonic acid which gives a well characterised oxime and a semicarbazide. On reduction with sodium amalgam, the author finds that isolauronic acid is readily converted into *dihydroisolauronic acid*, $C_9H_{14}O_3$ (m. p. 88°), a result differing somewhat from that of Koenigs and Meyer, who obtained in this way a lactone, $C_9H_{14}O_2$, melting at 47—50°, together with a substance melting at 80—81°, which they consider to be a mixture of two acids, $C_9H_{14}O_3$ and $C_9H_{16}O_3$.

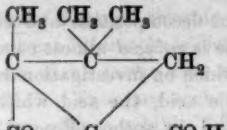
The author has further studied the action of oxidising agents on isolauronic acid, and finds that, under certain conditions, this acid is split up into dimethylsuccinic acid, $COOH\cdot C(CH_3)_2\cdot CH_2\cdot COOH$ and a ketonic acid, $C_8H_{14}O_3$, which melts at 51°.

This ketonic acid on oxidation is converted into $\alpha\alpha$-dimethylglutaric acid, $CO_2H\cdot C(CH_3)_2\cdot CH_2\cdot CH_2\cdot CO_2H$, and it therefore evidently has the constitution $CH_3\cdot CO\cdot C(CH_3)_2\cdot CH_2\cdot CH_2\cdot CO_2H$, and is identical with the acid previously obtained (Proc., 1896, **12**, 190), by oxidising β-camphylic acid.

A careful study of the results obtained in this long series of experiments on sulphocamphylic acid and the acids derived from it, seems to the author to clearly indicate that the constitutions of isolauronolic and isolauronic acids are most probably represented by the following formulæ.



Isolauronolic acid.



Isolauronic acid.

As sulphocamphylic acid on heating is resolved into isolauronolic acid and sulphuric acid, and on the other hand, isolauronolic acid, as was indicated in a previous communication (Proc., 1893, 9, 109) and has since been proved, when heated with sulphuric acid at 90°, is again converted into sulphocamphylic acid, it follows that the determination of the constitution of isolauronolic acid will throw most important light on the formula of sulphocamphylic acid, and on the remarkable changes which take place during the formation of this sulpho-acid from camphoric acid.

The discussion of these points and of their bearing on the constitution of camphoric acid, the author must reserve for a detailed description of his experiments, which he hopes soon to be able to lay before the Society.

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II. *Donations.*

Clowes, F., and Coleman, J. B. Quantitative Chemical Analysis. Fourth edition. Pp. xxiv + 583. London 1897.

From the Authors.

Fletcher, Thomas. The Commercial Uses of Coal Gas. Pp. 104. London 1897. From the Author.

Harcourt, A. G. Vernon, and Madan, H. G. Exercises in Practical Chemistry. Fifth edition revised by H. G. Madan. Pp. xvi + 598. Oxford 1897. From H. G. Madan, Esq.

Hewitt, J. T. Organic Chemical Manipulation. Pp. xi + 260, 63 illustrations. London 1897. From the Author.

Mawe, J. Instructions for the Management of the Blow-Pipe, and Chemical Tests. 3rd edition. Pp. 71. London 1822.

From C. E. Franck, Esq.

Mendeléeff, D. The Principles of Chemistry, translated from the Russian (6th edition) by G. Kamensky. Edited by T. A. Lawson. Vol. I., pp. xviii + 621; vol. II., pp. 518. London 1897.

From the Editor.

Newth, G. S. A Text-book of Inorganic Chemistry. 5th edition. Pp. xv + 669. London 1897. From the Author.

Sykes, W. J. The principles and practice of Brewing. Pp. xviii + 511. With plate and numerous illustrations. London 1897.

From the Author.

Walke, Willoughby. Lectures on Explosives. A course of lectures prepared especially as a manual and guide in the laboratory of the U.S. Artillery School. Pp. xvi + 435. 2nd edition. New York 1897.

From the Author.

Wilson, G. Inorganic Chemistry. New edition revised and enlarged by H. G. Madan. Pp. v + 535. London 1897.

From H. G. Madan, Esq.

Williams, R. P. Elements of Chemistry. Pp. vi + 412. Boston 1897. From the Publishers.

Gabba, L. Manuale del Chimico e dell' industriale. Pp. xvi + 442. Seconda edizione. (Manuali Hoepli.) Milano 1898.

Ghersi, I. Leghe Metalliche ed Amalgame. Pp. xii + 431 con 15 incisioni. (Manuali Hoepli). Milano 1898.

Vender, V. La Fabbricazione dell' Acido Solforico. Pp. v + 312 con 107 incisioni. (Manuali Hoepli). Milano 1897. From the Publishers.

Allen, Matthew. Outlines of a Course of Lectures on Chemical Philosophy. Pp. x + 70. London 1819.

Bergman, Torberni. Sciagraphia Regni Mineralis Secundum Principia Proxima Digesti. Editio prima Italica. Pp. 160. Florentiae 1783.

Davy, Humphrey. Outlines of a Course of Lectures on Chemical Philosophy. Pp. 54, and Sadler, John. An Explanation of the Terms used in Chemistry. Pp. 22. London 1804.

Dundonald, Earl of. A Treatise showing the Intimate Connection that subsists between Agriculture and Chemistry. Pp. vii + 252. London 1795.

Fourcroy, A. F. Élémens d'histoire naturelle et de Chimie. Cinquième édition. Vols. 1 and 5. Paris.

Oliver, William. A Practical Dissertation on Bath Waters. Pp. 136. London 1707. From S. G. Rosenblum, Esq.

Pamphlets.

Baker, R. T., and Smith, H. G. On the Presence of a True Manna on a "Blue Grass," *Andropogon annulatus*, Forsk. (Read before the Royal Society of N.S. Wales.) From the Authors.

Head, J. On Charging Open-hearth Furnaces by Machinery. Pp. 26. Reprint from the *Journal of the Iron and Steel Institute*, 1897. From the Author.

Head, J. The Coal Industry of the South-eastern States of North America. Excerpt from the *Transactions* of the Federated Institution of Mining Engineers, 1897. From the Author.

Jones, L. J. W. Ferric Sulphate in Mine Waters, and its action on metals. Pp. 9. Read before the Colorado Scientific Society, June 5, 1897. From the Author.

Latham, P. W. On the Synthesis and Molecular Construction of the Dead and Living Proteid. Pp. 28. Cambridge 1897. From the Publishers.

Long, J. H. On the Speed of Reduction of Ferric Alum by Sugar. Chicago 1897. From the Author.

Wardle, Sir Thomas, and Bell, P. Carter. On the Adulteration of

Silk by Chemical Weighting. Pp. 43. Read before the Society of Chemical Industry, April, 1897. From the Authors.

Wood, T. W. The Assay of Bullion, and Ellis, T. Flower. A Brief Account of the Malay Tin Industry. Chemical and Metallurgical Society of Johannesburg. February, 1897.

From T. J. McKillop, Esq.

At the next Meeting, on Thursday, November 18th, the following Papers will be received. The authors of those marked with an asterisk have announced their intention of being present.

* "On the decomposition of camphoric acid by fusion with potash or soda." By A. W. Crossley, M.Sc., Ph.D., and W. H. Perkin, jun., F.R.S.

"Experiments on the synthesis of camphoric acid." By W. H. Bentley, B.Sc., and W. H. Perkin, jun., F.R.S.

* "The action of magnesium on cupric sulphate solution." By Frank Clowes, D.Sc., and R. M. Caven, B.Sc.

* "Properties and relationships of dihydroxytartaric acid." By H. J. H. Fenton, M.A.

LIBRARY.

The attention of Fellows is called to the change of the hours during which the Library is open for consultation.

The Library is open for consultation and the issue of books from 10 a.m. to 6 p.m. (Saturdays 10 a.m. to 4 p.m.) and on the evenings of meetings from 7 p.m. to 9 p.m.

CERTIFICATES OF CANDIDATES FOR ELECTION.

N.B.—The names of those who sign from "General Knowledge" are printed in *italics*.

The following Candidates have been proposed for election. A ballot will be held on Thursday, December 2nd.

Annis, Ernest George,
Health Office, Town Hall, Huddersfield.

Physician and Surgeon (M.R.C.S. Eng., L.R.C.P. Lond., L.S.A. Lond., D.P.H., R.C.S. & P.). Medical Officer of Health and General Chemical Adviser to the Town Council of County Borough of Huddersfield.

Henry E. Roscoe.	S. G. Rawson.
Arthur P. Luff.	Frank Scudder.
Thos. Stevenson.	Henry Kenwood.

Ball, John, Ph.D., A.R.S.M.
18, Redshaw Street, Derby.

Engineer. Has studied Chemistry and Metallurgy for four years at the Royal College of Science, London, the Royal Saxon Mining Academy, Freiberg, and the University of Zurich. During a portion of the above time was engaged in research. Author of a paper dealing with the rate of solution of zinc in acids, *Proc. C.S.*, December 3rd, 1896; "Assaying at the Royal Saxon School of Mines," *Mining Journal*, October, 1895; also "The Serpentine and Associated Rocks of Davos," Zurich, 1897. Whitworth Scholar. De la Beche Medallist of the Royal School of Mines, London.

T. E. Thorpe.	W. C. Roberts-Austen.
W. Palmer Wynne.	A. Howard.

William A. Tilden.

Ball, William,
54, Stretton Road, Leicester.

Science Teacher. Teacher of Chemistry (Theoretical and Practical) for last eight years. For last six years, Teacher of Chemistry at the Alderman Newton's School, Leicester.

E. J. Cox.	Lewis Ough.
R. E. S. Richardson.	*W. W. Fisher.*

John Watts.

Beadle, Alec. Alfred,
Beadonwell, Belvedere, Kent.

Electro-Chemistry. Two years' course Electricity at Faraday House, Charing Cross; six months' course Analytical Inorganic Chemistry, under Mr. C. J. Wilson; three and a half years Assistant to Mr. James Swinburne, carrying on work of Chemical and Electro-chemical nature.

Chas. Fred. Cross.	Charles J. Wilson.
Clayton Beadle.	James Swinburne.
Dugald Clerk.	James Dewar.
Otto Hehner.	*Edward Bevan.*

Burland, Richard Oxley, J.P.,
Poolstock House, Wigan.

Manufacturing Chemist. Taken Certificates South Kensington. Member Society Chemical Industry. Manufacturing Chemist twenty years, Sulphate of Iron, Oxide of Iron, Oil, Paints, &c.

E. H. Saniter.	Arthur H. Tuer.
Wm. Jas. Orsman.	*Arthur Carey.*

Charles A. Kohn.

Cameron, Alexander McLean,
Daylesford, Victoria.

Director and Science Teacher School of Mines three years. Edinburgh University. Matriculated 1880, and attended usual courses of Chemistry, Botany, and Natural History for three years; also during same period attended the Chemical Laboratory of the Public Analyst to the City, J. Falconer King, and Extramural Lecturer; obtained Certificate of Merit. Melbourne University, 1891, obtained Certificate for Metallurgy (including Assaying). Government of Victoria, 1893, obtained highest grade Certificate for Chemistry, Metallurgy, and Assaying, with Honours in each, and the Education Department's Scholarships.

J. Dennant.	J. Falconer King.
Orme Masson.	*C. R. Blackett.*

A. W. Craig.

Clark, Owen Aly,
12, Abbeygate Street, Bury St. Edmunds.

Chemist. Associate Pharmaceutical Society Great Britain. Analytical and Consulting Chemist to Greene, King and Co., Limited, Westgate Brewery, Bury St. Edmunds. Analytical and Consulting Chemist to the Norwich Property Owners' Association.

Frank Browne.	Fredk. Johnson.
W. Watson Will.	*Thomas Tyrer.*

Arthur E. Barclay.

Clarkson, Alexander,

2, Waveney Crescent, Ballymena, Ireland.

Analytical Chemist. The Antrim Iron Ore Co., Ltd., Belfast. Seven years' experience as an Analytical Chemist. Two years as a Student, and 5 years as Assistant Chemist in the Laby's Parkhead Forge, Glasgow, and L.S. Co. Ltd., Motherwell.

R. R. Tatlock. — A. Humboldt Sexton.
John A. Craw. — Geo. Ritchie.

H. W. Dickinson.

Collingridge, Frank,

"Kenmore," Shepherd's Hill, Highgate, London, N.

Chemical Research Student. Bachelor of Science (London, 1895) Chemistry, Physics, Mathematics. Associate of Institute of Chemistry (1896).

William Ramsay. — N. T. M. Wilsmore.
Morris W. Travers. — J. Norman Collie.
J. Wallace Walker. — A. M. Kellas.

Crofts, James Murray,

"Richleigh," Gloucester.

Research Student of Emmanuel College. B.A. Emmanuel College, Cambridge. First Class Nat. Sciences Tripos Part I.; 2nd. Class Nat. Sciences Tripos, Part II. (Chemistry and Physiology). Inter. Science (London): Scholar of Emmanuel College.

G. D. Liveing. — W. J. Sell.
H. J. H. Fenton. — M. M. Pattison Muir.
S. Ruhemann. — R. S. Morrell.

George Embrey.

Crole, David,

Primrose Studios, Wellington Square, Chelsea, S.W.

Author. Carried out researches in India, &c., in the Chemistry of Tea; read a paper on that subject before the Society of Arts this year, and also written a technical work on "Tea." Have been a Student under, or worked in, the Laboratories of Professors Drinkwater, Page, Bayne, &c.

James Bayne. — Frederic Jas. M. Page.
Hubert E. Lindley. — *H. Wilson Hake.*

M. Kelway Bamber.

Daniell, John,

Council of Education Laboratory, Johannesburg, S.A.R.

Lecturer in Chemistry and Assaying to Witwatersrand School of Metallurgy. For 18 years Head Chemist and Head Assayer to Messrs. Nevill, Druce & Co., Llanelly, S. Wales. Lecturer in Chemistry

etc., at Llanelly under S. and A. Department. Now Director of the Witwatersrand School of Metallurgy.

Robert Wallace. Lionel. M Jones.
John R. Morgan. *J. Falconer King.*
George Beilby.

Dixon, Andrew James,
Dapto, N.S.W.

Head Chemist and Assayer to the Smelting Company of Australia. Three years a student at the Glasgow and West of Scotland Technical College with Profs. Mills and Dittmar. Passed as an Associate of the Institute of Chemistry in 1891, and became a Fellow in 1896. Studied Metallurgy for 1 year at the Royal School of Mines. Worked 3½ years as analyst with W. A. Dixon in Sydney. At present Head Chemist and Assayer to the Smelting Company of Australia.

Will. A. Dixon. William M. Hamlet.
Alexander Orr. Henry G. Smith.
A. J. Bersusan.

Guttmann, Oscar, Assoc. M. Inst. C.E., F.I.C.,
12, Mark Lane, London, E.C., and 18, Aberdare Gardens, N.W.

Consulting Engineer, engaged in the management and erection of explosives and chemical works for the last 23 years, author of various books and contributions to periodicals on explosives and other matters, member of council of the Society of Chemical Industry, etc., etc.,

Otto Hehner. John A. R. Newlands.
John Heron. Rudolph Messel.
Arthur R. Ling. C. A. Mitchell.
B. E. R. Newlands.

Hamilton, Robert,
11, Ibrox Place, Glasgow.

Science Teacher. Bellahouston Academy, Govan, Glasgow. Eight years Teacher of Chemistry and Physiography in above school. Certificated by Science and Art Department in Inorganic Chemistry (first Honours), Organic Chemistry, Physiography, Magnetism and Electricity, Geology, Mathematics (Glasgow University).

R. R. Tatlock. James Craig.
Hugh Manners. *James Robson.*
William Ralston. *Thomas Gray.*
John Wm. Biggart.

Harger, John,
The Nook, St. James' Mount, Liverpool.

I studied three years at University College, Liverpool, and took degree of B.Sc. with Honours in Chemistry in Victoria. Worked for

eighteen months at Heidelberg University, and took degree of Ph.D. Research on Succinic Acid Derivatives. Worked with Professor P. E. Frankland at Mason College, for one year, as Priestley Research Scholar—Research on Tartaric Acid Derivatives. I am an Associate of Institute of Chemistry of Great Britain and Ireland.

J. Campbell Brown. Charles A. Kohn.
R. E. Kenyon. Andrew Turnbull.
W. R. Innes.

Horseman, James Walter,
5, South Parade, Chelsea, London, S.W.

Demonstrator to Drs. Moritz and Morris, of 72, Chancery Lane. Intermediate Science, London. Two years' study at University College of North Wales, Bangor. One and half year's study at University College, London. Private Assistant to Professor Ramsay before holding present post.

William Ramsay. John Shields.
Morris W. Travers. N. T. M. Wilsmore.
J. Norman Collie. Geo. W. MacDonald.

Kelly, Charles,
Oakmere, Hawarden, Chester.

Science Teacher. 1883—93, Assistant Master; 1893—96, Exhibitioner, Royal College of Science, London; 1896 to present, Science Master.

William A. Tilden. W. Palmer Wynne.
Chapman Jones. Martin O. Forster.
James Bruce.

Lemmey, Tom,
Wellington College, Berks.

Assistant Master. B.A. Oxon. Honours School of Natural Science (Chemistry). Second Science Master at Wellington College.

H. Purefoy Fitzgerald, V. H. Veley.
W. W. Fisher. E. W. T. Jones.
John Watts. J. E. Marsh.

Maclaurin, James Scott,
Mount Eden, Auckland, N.Z.

Analytical Chemist. Author of the following papers in the *Transactions* of the Chemical Society: "The Dissolution of Gold in a Solution of Potassium Cyanide," 1893; "The Action of Potassium Cyanide Solutions on New Zealand Gold and Silver," 1895; "The Relative Weights of Gold and Silver dissolved by Potassium Cyanide

Solutions from Alloys of those Metals," 1896; "Double Sulphides of Gold and other Metals," 1896. B.Sc. 1891; First Class Honours 1892; D.Sc. 1897; all of New Zealand University. Science Scholarship of Royal Commission for 1851 Exhibition gained in 1895.

Fred D. Brown. Henry E. Armstrong.
J. A. Pond. *A. Vernon Harcourt.*
James Mactear. *Claude Vautin.*
D. A. Sutherland.

Macmullen, Alan,
82, James Street, Dublin.

Brewer at Messrs. A. Guinness, Son and Co., Ltd. Natural Science Scholar at Balliol College, Oxford. First Class in Chemistry, Natural Science School. Science Master at Wellington College, Berks. Is studying the science and practice of brewing.

A. Vernon Harcourt. John Conroy.
D. H. Nagel. Wm. Odling.
W. W. Fisher.

Mansford, Charles John Jodrell, B.A. London,
Lady Manners Grammar School, Bakewell.

Headmaster. Headmaster of Lady Manners Grammar School and Organised Science School. Engaged in teaching Chemistry since 1884.

A. S. Waterfield. William G. Boul.
R. W. Buttemer. *Samuel Rideal.*
G. E. Scott Smith.

Masters, Edward,
The Aloes, Hinckley Road, Leicester.

Science Teacher. Associate of the Royal College of Science, London (in Chemistry). Now Teacher of Chemistry and Physics at Alderman Newton's Higher Grade Science School, Leicester.

William A. Tilden. G. S. Newth.
Chapman Jones. W. Palmer Wynne.
James Bruce.

Mathews, John A.,
4, First Place, Brooklyn, N.Y.

Fellow in Chemistry, Columbia University, N.Y. Washington and Jefferson College (B.S. and M.S.) Three years Post-graduate in Columbia University (M.A.). Assistant in Assaying and Quantitative in Columbia, 1896—7; Fellow-Elect in Chemistry, 1897—8. Publications in journals:—*School of Mines Quarterly* (1894), "Carborundum"; *J. Amer. Chem. Soc.* (1896), "Phthalimid"; *J. Amer. Chem. Soc.* (1896), "Table of Factors" (with E. H. Miller); *J. Amer. Chem. Soc.* (1897), "On the Ferrocyanides of Zn and Mn" (with Dr. Miller); Lectured

to Brooklyn Institute of Arts and Sciences (1896). An extended *Review and Bibliography* (600 references) *of the Metallic Carbides* was recommended to the Smithsonian Institution for publication, and accepted by that Institution. It has not yet been published. The "Committee on Indexing Chemical Literature" of the American Association for the Advancement of Science which thus approved and recommended my work consisted of H. Carrington Bolton, H. W. Wiley, Francis W. Clarke, A. R. Leeds, A. B. Prescott, and Alfred Tuckerman.

Charles F. Chandler. Peter T. Austen.
Jas. S. C. Wells. H. T. Vultè.
James H. Stebbins, Jun. *Thos. P. Wiltshire.*
S. A. Goldschmidt. *J. H. Wainwright.*
V. Coblentz. *Wm. Jay Schieffelin.*

Moon, Philip George Gregory,
129, Rosary Road, Thorpe, Norwich.

Chemist in charge, British Gas Light Company, Norwich. Chemist to the British Gas Light Company. Formerly student for 3 years at the East London Technical College. Assistant Chemist for 3 years at Messrs. Martineau's sugar refinery, London; 1st Honours and Medal, Inorganic Chemistry, South Kensington, 1894.

Sydney Steel. J. Theo. Hewitt.
Francis Sutton. A. P. Laurie.
F. Napier Sutton. *Bernard Dyer.*

Mooney, Joseph John,
34, Easter Road, Edinburgh.

Surgeon and Apothecary. L.S.A. London, L.A.H. Dublin, worked for 6 months in the Pharmaceutical Laboratory of Owens College under Mr. Wm. Elborne, and for 6 months in the Laboratory of Mr. King, Edinburgh, City Analyst. Author of "Chemical Processes relating to Water, Air, Food, and Drugs." In course of publication by Thin, Edinburgh.

William Elborne. J. Falconer King.
Eugen Blume. *J. Watson Napier.*
G. H. Gemmell.

Philip, James Charles,
16A, Merton Road, Victoria Road, Kensington, W.

Student. Graduated B.Sc. at Aberdeen University, 1895; Ph.D. of Göttingen, 1897. Published in the *Zeitschrift für physik. Chemie*, September, 1897, article on "Das dielectrische Verhalten flüssiger Mischungen."

F. R. Japp. T. S. Murray.
Henry E. Armstrong. F. Stanley Kipping.
Gerald T. Moody.

Reid, Alexander Ferguson,

Stair Bridge, Stair, Ayrshire.

Technical Chemist. (1) Some time Chemical Assistant to Hugh Dickie, B.A., LL.D., of Kilmarnock. (2) Three years in the laboratories of Messrs. Wallace, Tatlock and Clark, City Analysts, Glasgow. (3) Studied Chemistry at the Glasgow and West of Scotland Technical College under Professor A. H. Sexton F.R.S.E., F.I.C., ; Professor G. G. Henderson, D.Sc., M.A., F.I.C., ; Professor A. Schloesser, Ph.D., M.Sc. F.I.C. (4) Five years Chemist to the Cassel Gold Extracting Company of Glasgow. (5) Nearly three years Chemist to Mr. Montgomerie, Stair, N.B. (6) Contributions to Chemical Literature :—*Chemical News*, vol. 57, p. 39, vol. 65, pp. 68, 125 ; vol. 66, p. 166 ; vol. 67, p. 159, &c. *Zeitschrift fur analytische Chemie*, vol. 32, part 4. *Journal of the Chemical Society*, 1892, p. 1027 (Abstracts).

G. G. Henderson.	Wm. Rintoul.
Horatio Ballantyne.	John Clark.
R. R. Tatlock.	John S. MacArthur.

A. Humboldt Sexton.

Roberts, Ernest Henry,

Hollydale, Allfarthing Lane, Wandsworth, S.W.

Chemist, Dairy Supply Company, Limited. Two and a half years Liverpool College of Chemistry, 7 years assistant to Dr. Bernard Dyer.

Bernard Dyer.	Sydney Steel.
Otto Hehner.	Edward Bevan.
J. F. H. Gilbard.	*Charles E. Cassal.*

Simpson, Edward Sydney, B.E.

34, Pier Street, Perth, West Australia.

Government Mineralogist and Assayer. Student Mining School University of Sydney, 1892—1895 ; 1st Honours and Slade Prize for Chemistry, 1893 ; 1st Honours and Caird Scholarship for Chemistry, 1894 ; Bachelor of Engineering with Honours, 1895 ; Researches on Russell Process in 1895 ; Assistant Assayer and Acting Analyst, Mt. Morgan G.M. Co., 1896—97.

A. Liversidge.	J. A. Schofield.
James Taylor.	*John C. H. Mingaye.*

John M. Thomson.

Smith, Robert Francis Wood,

89, Bartholomew Close, E.C.

Bacteriologist and Consulting Chemist. Special Chemistry Course (three years) at City Guilds Technical College at South Kensington.

Late private assistant to Prof. A. A. Kaultack at St. Bartholomew's Hospital Path. Lab.; author of paper, "Vibrio Tonsillaris," *Centralblatt für Bakteriologie*, etc.

Gerald T. Moody.	F. Stanley Kipping.
Julian L. Baker.	R. C. T. Evans.
Henry E. Armstrong.	Arthur R. Ling.

Southern, Thomas, Junr.,

2, Cherry Mount, The Cliff, Higher Broughton, Manchester.

Manufacturing Chemist. Studied Chemistry, 1883—1886, under Mr. Wilson, of Manchester Grammar School, and 1886 under Mr. G. H. Hurst, Analytical and Consulting Chemist, Manchester. Subsequently 2 years at Owens College, Manchester. Now Chemist to the Wheathill Chemical Works, Salford, where I have had inside management of the works and superintendence of various alterations and improvements during the past 6 years. Member of the Society of Chemical Industry.

Christopher Wilson.	George H. Hurst.
J. Carter Bell.	George J. Allen.

R. J. Flintoff.

Steel, Frederick William,

Tamunua, Navua River, Fiji.

Analytical Chemist. Student, Science and Art Dept., local (Glasgow and Greenock) Classes. Student under Prof. J. M. Milne, Ph.D., F.I.C. (St. Mungo's College, Glasgow). Student under Prof W. Dittmar, LL.D., F.R.S. (G. & W. S. Technical College). Three years Chemist to the Fiji Sugar Co., Ltd., and at present still holds this position.

Thos. Steel.	T. U. Walton.
T. L. Patterson.	*John Wm. Biggart.*

Geo. Patterson.

Stephens, Michael Edmund,

Avenue House, Finchley.

Writing Ink Manufacturer, partner in the firm of Henry C. Stephens of Aldersgate Street. The Candidate has had the Technical Management and direction of the laboratory and works for the past 11 years.

James Dewar.	Henry E. Armstrong.
William Crookes.	Henry C. Stephens.
John A. R. Newlands.	Boverton Redwood.
E. Frankland.	*F. A. Abel.*

Stubbs, George,

Arnside, Hertford Road, East Finchley, N.

A Student at the Royal College of Science, 1887–8. Analyst in the Government Laboratory, London. For seven years assistant teacher of Organic Chemistry at the Birkbeck Institution.

T. E. Thorpe.	R. Bannister.
H. J. Helm.	E. Grant Hooper.
J. Woodward.	C. Proctor.

Tripp, Edward Howard,

Kent House, Blackheath Hill, S.E.

Ph.D. (Marburg). Four-and-a-half years' study in Germany. Joint author with Prof. Zincke of an original investigation of "Ketobromides in the asym. Xylenol series," Member of the "Deutsche Chemische Gesellschaft," Honorary Demonstrator at the Central Technical College, City and Guilds of London Institute.

Thomas Tyrer.	Wm. Martindale.
Henry E. Armstrong.	Aug. Schloesser.
Rudolph Messel.	*David Howard.*

Turner, John Scriven,

20, Bury Street, Bloomsbury, London, W.C.

Assistant to J. Kear Colwell, Esq., Public Analyst, Clerkenwell Town Hall, Rosebery Avenue, London, E.C. Studied Chemistry at University College School under Temple Orme, Esq., and for two years in the laboratories of the Pharmaceutical Society under Professors W. R. Dunstan, F.R.S., F.I.C., and J. Attfield, F.R.S., F.I.C. For the past twelve months assistant to J. K. Colwell, F.I.C., Public Analyst for St. Giles', Holborn and Clerkenwell.

J. Kear Colwell.	Wyndham R. Dunstan.
John Attfield.	*J. Norman Collie.*

Charles E. Cassal.

Viccajee, Framjee Khurshedjee,

Hyderabad, Deccan (India), H.H. the Nizam's State.

Hyderabad Civil Service, H.H. the Nizam's Mint. Studied Chemistry at the Nizam's College, Hyderabad, Deccan (India) (2 years' course) served probation at the Assay Office, Bombay Mint, for about 12 months. In charge of Assay Work at H.H. the Nizam's Mint (1894–96); went through a course of Metallurgy and Assaying at the Royal School of Mines (1896–97), London.

W. C. Roberts-Austen.	Henry C. Jenkins.
Ernest A. Smith.	F. W. Bayly.

T. K. Rose.

Vinter, Percy John,
Wesley College, Sheffield.

Schoolmaster. Second Class Science Tripos, 1893, Cambridge; Chemistry one of the three subjects taken. Further work done in Organic preparations in the University Laboratories. Now Senior Science Master, Wesley College, Sheffield; formerly Science Master, Blairlodge School, Scotland.

S. F. Dufton. Alexander Scott.
F. L. Overend. *W. Carleton Williams.*
G. T. W. Newsholme.

While, Arthur James,
Whinsfield, Barrow-in-Furness.

Analytical Chemist. First Class Metallurgy and Assaying School of Mines, London. Eighteen months Head Chemist to Barrow Hæmatite Steel Co.

W. C. Roberts-Austen. F. W. Bayly.
T. K. Rose. Ernest A. Smith.
Henry C. Jenkins.

Young, Francis Samuel,
Mile Hill School, London, N.W.

Science Master, Mill Hill School; M.A. Oxon. Degree in Final Honour, School of Chemistry. Research with Dr. Ruhemann in 1894. Teacher and Lecturer on Chemistry at Mill Hill School, London, N.W., since 1894.

V. H. Veley. W. W. Fisher.
J. E. Marsh. John Watts.
J. Addyman Gardner. S. Ruhemann.

RICHARD CLAY AND SONS, LIMITED, LONDON AND BUNGAY.

Issued 30/11/1897.

PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

EDITED BY THE SECRETARIES.

No. 184. Session 1897–8.

November 18th, 1897. Professor Dewar, F.R.S., President, in the Chair.

Messrs. W. J. Elliott, H. S. Elworthy, F. F. de Morgan, Frank Moul, A. Harden, and Charles E. Browne were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Cecil Joslin Brooks, 24, Wood Street, Woolwich; Charles Henry Burge, Iddesleigh Crescent Road, Kingston Hill, S.W.; M. J. Cannon, 101, The Chase, Clapham Common, S.W.; William Ranson Cooper, M.A., B.Sc., 87, Upper Tulse Hill, S.W.; Frederick Robertson Dodd, 1, Wesley Street, Liverpool; Jules Fuerst, 23, Marlborough Road, N.W.; James Brown Reid, 6, Southfield Terrace, Skepton; Harold Charles Sayer, Devon Villa, Summerhill Road, Dartford.

The PRESIDENT announced that he had received a letter from Sir Fleetwood Edwards stating that he had been commanded by the Queen to forward to him a Medal in commemoration of the 60th Anniversary of Her Majesty's reign.

Of the following papers those marked * were read.

***118. "On the decomposition of camphoric acid by fusion with potash or soda." By Arthur W. Crossley and W. H. Perkin, jun.**

The authors find that by the action of fused potash on camphoric acid a very complicated mixture of acids is obtained. The volatile portion consists of acetic, propionic, isobutyric, isovaleric and

methylisopropylacetic acids, together with acids of the formulæ $C_6H_{13}CO_2H$, $C_7H_{15}CO_2H$ and $C_8H_{17}CO_2H$, of which the constitution is doubtful. The non-volatile acids consist of pimelic (isopropylsuccinic) acid and a new substance, dihydrocamphoric acid.

Dihydrocamphoric acid, $C_{10}H_{18}O_4$, crystallises in nodular masses melting at 105—106°, and on oxidation with dilute nitric acid yields succinic acid, oxalic acid, and an acid of the formula $C_8H_{14}O_4$, which is in all probability the $a\beta\beta$-trimethylglutaric acid described by Balbiano.

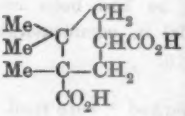
On treatment with acetic anhydride, dihydrocamphoric acid is converted into its anhydride, which, when heated to boiling, decomposes with elimination of carbon dioxide and formation of a cyclic ketone of the formula $C_9H_{16}O$. *Dihydrocamphoketone* is a liquid boiling at 180—181° and smelling strongly of peppermint. It forms a liquid ketoxime and a semicarbazone melting at 202—203°.

The results obtained on fusing camphoric acid with caustic soda differ markedly from the above. The lower volatile fatty acids appear to be the same as those obtained from caustic potash, but there is also present an unsaturated acid of the formula $C_8H_{15}CO_2H$.

The acids not volatile in steam consist of large quantities of pimelic acid and some unchanged camphoric acid, together with two new acids, pseudocamphoric acid, $C_{10}H_{16}O_4$ and an acid of the formula $C_9H_{16}O_4$, boiling at 254—257° at 50 mm.

Pseudocamphoric acid crystallises from water in colourless, six-sided plates with bevelled edges, usually grouped together in the form of stars, and melts at 119—120°. It forms a crystalline anhydride melting at 52—53° and an anilic acid melting at 208°. A further difference from its isomeride *d*-camphoric acid is that when treated with sulphuric acid it does not evolve carbon monoxide forming a sulphonic acid.

The authors explain the results of the action of fused alkalis on camphoric acid and deduce constitutional formulæ for the various compounds obtained on the assumption that camphoric acid is represented by the formula



***119 "Experiments on the synthesis of camphoric acid." By W. H. Bentley and W. H. Perkin, jun.**

The authors have attempted to prepare an acid of the constitution suggested (Proc., 1896, 12, 189) as a probable formula for camphoric acid (see preceding abstract). They prepared isobutylmethylhydroxy-

glutaric acid, $Me_2\cdot CH^*\cdot CH_2\cdot CH(CO_2H)\cdot CH_2\cdot C(CO_2H)Me\cdot OH^*$, but did not succeed in eliminating water in the direction desired (at the points * *), the product in most of the experiments being the lactone-acid, $Me_2\cdot CH\cdot CH_2\cdot \underset{CO}{CH}\cdot CH_2\cdot \underset{O}{C}\cdot Me\cdot CO_2H$, or one of its derivatives.

The following substances were prepared during the course of the work.

Ethylic bromisobutylacetate, $(Me_2)\cdot CH\cdot CH_2\cdot CHBr\cdot CO_2Et$, an oil boiling at 100—103° (17 mm.).

Ethylic acetylisobutylsuccinate, $\begin{matrix}Me_2\cdot CH\cdot CH_2\cdot CH\cdot CO_2Et\\ Me\cdot CO\cdot CH\cdot CO_2Et\end{matrix}$, prepared by the action of ethylic bromisobutylacetate on ethylic sodioacetoacetate. It is a colourless oil boiling at 160° (25 mm.), and when hydrolysed with dilute hydrochloric acid or sulphuric acid yields *isobutylsuccinic acid*, $Me_2\cdot CH\cdot CH_2\cdot CH(CO_2H)\cdot CH_2\cdot CO_2H$, m. p. 109°. When hydrolysed with concentrated hydrochloric acid, however, *isobutyllevulinic acid*, $Me_2\cdot CH\cdot CH_2\cdot CH(CO_2H)\cdot CH_2\cdot COMe$, is formed. This is a colourless oil boiling at 190° (30 mm.), and yielding a semi-carbazone melting at 192°: bromine, in the presence of potash, oxidises it to isobutylsuccinic acid.

Isobutyllevulinic acid readily unites with hydrogen cyanide, forming *isobutylhydroxycyanovaleric acid*, $Me\cdot C(OH)(CN)\cdot CH_2\cdot CH(C_4H_9)\cdot CO_2H$, which crystallises with $1H_2O$ in needles melting at 95—96°. This acid on distillation yields the corresponding *lactone*,

$$\begin{matrix}Me\cdot C(CN)\cdot CH_2\cdot CH\cdot C_4H_9\\ O\text{———}CO\end{matrix}$$

, m. p. 53°.

When an alcoholic solution of the hydroxy-cyano acid is saturated with hydrogen chloride, it is hydrolysed and converted into the ethereal salt of *isobutylmethylhydroxyglutaric acid*,

$$Me\cdot C(OH)(CO_2Et)\cdot CH_2\cdot CH(C_4H_9)\cdot CO_2Et,$$

on distillation, this loses alcohol, forming the ethereal salt of the *lactone* of *isobutylmethylhydroxyglutaric acid*,

$$\begin{matrix}Me\cdot C(CO_2Et)\cdot CH_2\cdot CH(C_4H_9)\\ O\text{———}CO\end{matrix},$$

which is an oil boiling at 168° (17 mm.). This on hydrolysis with alcoholic potash is converted into *isobutylmethylhydroxyglutaric acid*, $Me\cdot C(OH)(CO_2H)\cdot CH_2\cdot CH(C_4H_9)\cdot CO_2H$, a crystalline acid melting at 134° with elimination of water and formation of the *lactone*,

$$\begin{matrix}Me\cdot C(CO_2H)\cdot CH_2\cdot CH\cdot C_4H_9\\ O\text{———}CO\end{matrix}$$

(m. p. 80°)

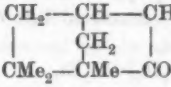
*120. "Synthesis of an isomeride of camphoronic acid." By S. B. Schryver, Ph.D.

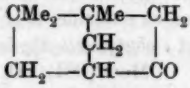
The compound, $CO_2H \cdot CH(Me)CH_2 \cdot C(CH_2 \cdot CO_2H)(Me) \cdot CO_2H$, was synthesised by acting on methylacrylic ester, $CH_2 : C(Me)CO_2Et$, with sodiomethylmalonic ester. The addition product thus obtained, having the formula $(CO_2Et)_2C(Me) \cdot CH_2 \cdot CNa(Me)CO_2Et$, instead of being isolated, was acted on by iodacetic ester. Among the resulting products was the compound $(CO_2Et)_2C(Me)CH_2 \cdot C(CH_2 \cdot CO_2Et)(Me) \cdot CO_2Et$, which on hydrolysis gave an acid of the required formula. This was isolated by means of its lead salt, which is insoluble in acetic acid, in the form of a syrup, and this on treatment with nitric acid gave a crystalline oxy-acid having the formula $C_9H_{14}O_7$. It is, therefore, an isomeride of camphoronic acid.

Discussion.

Dr Kipping said that it was very difficult to criticise papers which, like those read by Drs. Crossley, contained so many new and important facts relating to substances of somewhat complex constitution. It seemed to him, however, that all the results obtained by Dr. Crossley and Dr. Perkin in their study of the substances produced by fusing camphoric acid with potash, could be explained on the basis of Bredt's formula; such an opinion might of course be altered after carefully examining the details of the work as laid out in the published papers.

Dr. Forster pointed out that the formula for camphoric acid employed by Drs. Crossley and Perkin appears to involve the expression of the constitution of camphor by one of the formulæ





The behaviour of camphoroxime on dehydration, and the isomerism of two series of campholenic derivatives, seem to render the second expression the more probable of the two, but before either could be accepted, an explanation must be furnished of the changes involved in the production of such compounds as cymene and carvacrol from camphor—changes which, it must be remembered, are readily explained by Bredt's formula.

The production of the acid, $CHMe_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CHMe \cdot CO_2 \cdot H$, obtained by the authors by fusing camphoric acid with alkali, harmonises with the new camphoric acid formula, but it must not be overlooked that Bredt's formula for camphoric acid affords an equally plausible explanation.

Dr. CROSSLEY, in reply, said that the main evidence for accepting the formula proposed by Professor Perkin was embodied in his paper on sulphocamphylic acid, which had not yet been published in detail. Whilst the production of most of the compounds described by Professor Perkin and himself admit of explanation by Bredt's formula, it does not account for the formation of $\alpha\alpha\beta\beta$-tetramethyladipic (dihydrocamphoric) acid.

***121. "The action of magnesium on cupric sulphate solution." By Frank Clowes, D.Sc., and R. M. Caven, B.Sc.**

The authors have examined the action of magnesium on solutions of cupric sulphate of different strengths, both at atmospheric temperature and at a temperature near their boiling point. They find that the evolution of hydrogen which always takes place is accompanied by the precipitation of a mixture of cuprous oxide and metallic copper in proportions which vary with the conditions of the experiment.

When a dilute solution of cupric sulphate is employed, the above mentioned products are accompanied by a quantity of a green substance, which consists of a mixture of basic hydrated sulphates of copper and magnesium. This substance was observed to form when a saturated solution of cupric sulphate was employed, but it was decomposed again before the reaction was completed.

The time of the reaction varies from ten minutes in the case of a hot strong solution of cupric sulphate to several days, or even a week, when a dilute solution is employed at atmospheric temperature.

The quantities of the three reduction products, cuprous oxide, copper, and hydrogen, were determined under various conditions. A volumetric process depending upon the use of potassium permanganate was employed for the estimation of the cuprous compound when it occurred together with the basic sulphate of copper and magnesium before mentioned.

The authors found in each case which they investigated that the sum of the magnesium equivalents of the cuprous oxide, copper, and hydrogen obtained agrees very closely with the amount of magnesium employed in the experiment. The magnesium is therefore proved to have displaced from the solution of cupric sulphate, substances which are chemically equivalent to it, though only a small and variable proportion of these substances consists of metallic copper. The authors have shown that the nature of the reaction is not influenced by the presence of slight impurities in the cupric sulphate employed by carrying out similar experiments with a specimen of the salt obtained by six successive recrystallisations of a sample which was originally almost pure. Pickering's observation of the formation of a

basic sulphate of copper by the decomposition of a solution of cupric sulphate by boiling, has been incidentally confirmed, but the formula which the authors attribute to this compound is $4CuSO_4,7Cu(OH)_2,H_2O$.

NOTE—*24th November.*—The authors have now referred to the paper by Commaille (*C. R.*, 1866, **63**, 556), and they find that an equation is given which is supposed to represent the reaction between magnesium and cupric sulphate solution. This equation, when it is put into modern form and corrected for an obvious error, reads as follows: $6CuSO_4 + 5Mg + 3H_2O = 5MgSO_4 + (3CuO,SO_3) + Cu_2O + Cu + 3H_2$.

No details are given as to the temperature or the strength of the cupric solution which acted on the magnesium, nor are the analytical data stated upon which the above equation is founded. It will be noticed that the formation of basic magnesium compounds is not accounted for in the above equation. The authors consider that the results of their own analyses and examination prove that the composition of the basic sulphate of copper is variable, but that it does not correspond to the above formula, and certainly occurs in the condition of hydroxysulphate. They have never found that the proportion between the quantities of cuprous oxide and metallic copper is such as can be definitely represented by means of an equation, but rather that it varies within wide limits under different experimental conditions.

It will therefore appear that Commaille's imperfect study and statement of the reaction may well be supplemented by a more complete investigation.

The authors desire to place on record the fact that, when zinc acts upon a cold solution of copper sulphate, small bubbles of gas are evolved; and that when a hot solution of cupric salt is employed, an appreciable quantity of hydrogen can be collected, and cuprous oxide is found in the residue. They intend to study this reaction in detail.

DISCUSSION.

Professor TILDEN remarked that the work of the authors had been anticipated by the experiments of Commaille, who had published thirty years ago the results of an inquiry into the action of magnesium on neutral metallic salts, including copper sulphate.

When magnesium is immersed in an aqueous solution of copper sulphate free from acid, the action seemed to take the following course. First, there was a precipitation of spongy, metallic copper, which, in contact with the magnesium, gave a couple capable of decomposing water at common temperatures. Hydrogen was then evolved, and a crust of magnesia formed on the surface of the metal. The copper

salt was locally reduced by the hydrogen to the cuprous state, and this, in the presence of the magnesium oxide, led to the precipitation of cuprous oxide and of a basic cupric salt. The green precipitate formed therefore consists of magnesia and basic cupric salt, the proportion varying according to the temperature and strength of the solution. This hypothesis is borne out completely by the results both by Commaille and the authors of the paper, and serves to account for the apparent inactivity of the magnesium which is mechanically protected by the crust which forms upon its surface. The speaker had tested the suggestion that the metal was rendered inactive by a film of hydrogen and had come to the conclusion that this was not the case.

Professor CLOWES said that the origin of the investigation dated back some two years, the irregular action of magnesium on the cupric solution having been noticed in the course of experiments made in connection with a laboratory curriculum which he was then drafting for elementary students. It was anticipated that the reaction of magnesium on cupric sulphate might serve to establish the relative chemical values of copper and magnesium, but this was found to be impracticable owing to the evolution of a large amount of hydrogen. If such irregular actions occurred, instead of the simple replacement of one metal by another in solutions of its salts, it would seem that this method of determining chemical equivalents was not of general application.

Mr. CAVEN, in reply, said he regretted that he had overlooked the paper by Commaille on this subject to which Dr. Tilden referred.

It seems improbable that cuprous salt is formed by the reducing action of nascent hydrogen upon the cupric salt in the solution. This would lead to the formation of free sulphuric acid, which would decompose the cuprous oxide formed at the commencement of the reaction into cupric sulphate and metallic copper. If nascent hydrogen reduces the cupric salt at all, it can only produce metallic copper. Sulphuric acid would be liberated in this case also, though not in immediate contact with cuprous oxide. It may be that the process of solution of the magnesium hydroxide and basic copper salt which occurs at the close of the reaction in concentrated solutions, depends upon the action of the free acid thus produced.

The authors suggest that the magnesium reduces the cupric solution directly, producing cuprous oxide and hydrogen in the following manner, the proportion of the hydrogen evolved in the gaseous state being dependent upon the conditions of the experiment:
$2Mg + 2CuSO_4 + H_2O = 2MgSO_4 + Cu_2O + H_2$.

Some such reaction as this, proceeding simultaneously with the action of the couple, may account for the immediate formation of cuprous oxide,

and the vigorous evolution of hydrogen at the moment of immersion of the magnesium. The action of the magnesium-copper couple on the water is not in itself sufficient to account for the very large quantity of hydrogen which is obtained, or for the rapidity with which it is produced, since, when the couple acts upon pure water, the hydrogen is evolved only very slowly. This view of the origin of the cuprous oxide is borne out by the fact that it occurs, together with metallic copper, quite from the commencement of the reaction, and that the formation of hydrogen appears to begin directly the magnesium is plunged into the solution. This would not be the case if the formation of a metallic couple were necessary for the evolution of the gas.

There is no cessation in the evolution of gas during the course of the reaction under any circumstances. The length of time necessary for the completion of the reaction in dilute solutions is undoubtedly due to the mechanical protection of the magnesium by the deposit, as Professor Tilden suggested.

*122. "Properties and relationships of dihydroxytartaric acid." By Henry J. Horstman Fenton, M.A.

Bearing in mind the highly interesting constitution of dihydroxytartaric acid, and the close relation which has been shown to exist between this acid and dihydroxymaleic acid, a further investigation of its properties appeared to be desirable, especially as the free acid appears to have been scarcely studied.

It is now found that the free acid may very easily be prepared in a pure state by oxidation of dihydroxymaleic acid in presence of water. The yield is over 70 per cent. of that demanded by theory. The dry acid shows no tendency to lose water at 90°. In aqueous solution, the acid decomposes when heated into tartronic acid and carbon dioxide. This reaction affords a very convenient method for the preparation of pure tartronic acid, the yield being 97 per cent. of that theoretically obtainable. On titration with alkalis at 0° dihydroxytartaric acid behaves normally as a dibasic acid. But the results obtained at the ordinary temperature with caustic alkalis, using phenolphthalein as indicator, are considerably higher, being intermediate between those required for a di- and a tri-basic acid. These high results are shown to be due to the partial decomposition of the salts formed into tartronates and carbon dioxide.

By careful treatment with certain reducing agents dihydroxytartaric acid may be reduced to dihydroxymaleic acid or its isomeride. Zinc, in calculated quantity, and dilute acid reduces it to the β-form. Hydro-

gen bromide reduces it to dihydroxymaleic acid (α-form) with liberation of free bromine.

The reaction $C_4H_4O_6 + 2H_2O + Br_2 = C_4H_6O_8 + 2HBr$ is in fact a reversible one, the final distribution depending upon the masses of the reacting substances and perhaps somewhat on the temperature.

***123. "The molecular association of liquids and its influence on the osmotic pressure." By Holland Crompton.**

In a paper which I recently had the honour of bringing before this Society (Trans., 1897, 71, 925), I contended that the molecular association of liquids exercises an influence on their osmotic pressure, and endeavoured to show how this influence may be taken into account. My attention has been drawn to the fact that Planck, more especially, has long since proved that association could have no effect on the osmotic pressure of liquids (see the discussion between Planck and Wiedemann, *Zeit. physik. Chem.*, 1888, 2, 241, 343). This being the case, I wish to offer the following brief criticism of Planck's results.

In his *Vorlesungen über Thermodynamik* (Leipzig, 1897), Planck deduces on p. 235 the following formula for the osmotic pressure of a dilute solution $P = \frac{R\theta}{n_0 m_0 v}(n_1 + n_2 + n_3 + \ldots\ldots)$. Here R is the constant of the gas equation, θ the absolute temperature, $n_1 + n_2 + n_3 + \ldots = n$ the number of dissolved molecules, n_0 the number of molecules of the solvent, m_0 its molecular weight, and v its specific volume (volume of unit weight). Since $n_0 m_0 v = V$ is practically the whole volume of the solution $P = R\theta n/V$. This is, of course, van't Hoff's equation for the osmotic pressure, and it is argued that the product $n_0 m_0 v$ being simply the total volume of the solution, the pressure is independent of any change produced by association in m_0. In other words, as long as V is constant P will remain constant, no matter what the value of m_0.

The nature and derivation of this relationship will perhaps be best understood if we suppose that we have two gases, and that n molecules of the first are dissolved in, or mixed with, n_0 molecules of the second. The partial pressure of the first gas in the mixture is $n/(n_0 + n)$ of the total pressure, or if n is small in comparison with n_0, we may say n/n_0 of the pressure of the second gas. The pressure of this latter is RT/V_0, and in order that R may have a fixed value, let V_0 be the molecular volume $m_0 v_0$ of the gas, where m_0 is its molecular weight, and v_0 its specific volume. The partial pressure of the dissolved gas then becomes $p = RTn/n_0 m_0 v_0$ or, since $n_0 m_0 v_0 = V_0$, the whole volume of the solvent gas, $p = RT/nV_0$.

These equations for the partial pressure of a gas present in a dilute state in any gaseous mixture are identical in form with those of Planck for the osmotic pressure of dilute solutions. It follows then that we have apparently only to liquefy the solvent gas, to substitute the molecular volume of the resulting liquid solvent for that of the gaseous solvent, and the partial pressure of the dissolved gas then becomes its osmotic pressure in the solution.

The result is not surprising, for it is obtained by a practical reversal of Planck's line of argument. It will be found (*loc. cit.*, p. 215) that, in his treatment of the thermodynamics of dilute solutions, he adopts the view that any such solution could be completely gasified without any change in the values of n and n_0, and, of course, the osmotic pressure of the dissolved compound in the solution would then become the partial pressure of the dissolved gas in the gaseous mixture. But the view that a solution could be completely gasified without any change of a permanent character in the values of n and n_0 cannot be regarded as justifiable in the light of all the recent work on the molecular condition of liquids. And although it is not surprising to find that, starting with this view, Planck subsequently comes to the conclusion that association of the solvent does not influence the osmotic pressure of a solution, the reasoning evidently moves too completely in a circle to carry much conviction with it.

For, in order to ascertain what effect a change due to molecular association in the solvent would have on our formulæ, let us first take the case of the mixed gases, and suppose the gas we term the solvent to be one, say, like nitrogen dioxide, NO_2, which undergoes association as the temperature falls. Such association will bring about a change of m_0 to xm_0, of n_0 to n_0/x, and of v_0 to v_0/x, if x represents the degree of association (factor of association) for any temperature T. The partial pressure of the dissolved gas now becomes $p = x\mathrm{R}\mathrm{T}n/n_0m_0v_0$, or since $n_0m_0v_0 = \mathrm{V}_0$, $p = x\mathrm{R}\mathrm{T}n/\mathrm{V}_0$. Hence, although when a gas is dissolved in any other gas and is present only in a dilute condition, its partial pressure will, under normal conditions follow the law that $p\mathrm{V}_0 = n\mathrm{R}\mathrm{T}$ if association of the solvent sets in, the law for perfect gases no longer holds, but the relationship becomes $p\mathrm{V}_0 = xn\mathrm{R}\mathrm{T}$ where x represents the factor of association of the solvent for the temperature T.

In fact, the partial pressure of the dissolved gas is, under the above conditions, dependent on the volume occupied by the solvent. Under normal conditions, the solvent obeys the usual gas equation, and the partial pressure therefore alters in accordance with this relationship. But if association or dissociation of the solvent sets in, the gas equation will not immediately apply, but will require a suitable modification, and this modification will hold also for the partial pressure formula.

Now the osmotic pressure of a dilute solution presents an analogous case. As long as the solvent is a monomolecular one we may accept Planck's reasoning and hold that the osmotic pressure follows the law $P = nR\theta/n_0 m_0 v$. But suppose that the solvent begins to undergo association, so that for any given temperature θ a change of m_0 to xm_0 has taken place. At the same time n_0 changes to n_0/x, and a simultaneous change will be found to have taken place in v. This last change has, it seems to me, been entirely overlooked up to the present, although any one who gives the matter a moment's consideration cannot fail to admit that an associated liquid would not have the density of the same compound in the monomolecular condition. All the evidence at present points to the conclusion that association increases the density of a liquid, and that consequently association would alter the value of v to v/a. The precise magnitude of a cannot at present be ascertained (unless perhaps with the aid of Traube's investigation of the molecular co-volume), but its value is probably not far removed from that of x. The osmotic pressure then of any dilute solution, the solvent of which is undergoing association, would be given by $P = anR\theta/n_0 m_0 v$, or since $n_0 m_0 v = V$, by $P = anR\theta/V$, an expression that is similar to the partial pressure formula. While, then, the osmotic pressure of any substance in solution in a monomolecular solvent follows the gas equation $PV = R\theta$, if the solvent is one which is undergoing association or dissociation, the equation for the osmotic pressure becomes $PV = aR\theta$.

And here another point which has apparently always been overlooked by those who contend that association of the solvent does not influence the osmotic pressure may be alluded to. It has been usual, hitherto, to compare with one another two stable systems, one of which is assumed to contain a monomolecular solvent and the other the same solvent in the associated condition and to show that the gas equation $PV = R\theta$ applies to each. The comparison, however, should not be between a monomolecular and an associated solvent, but between a monomolecular and an associating solvent, *i.e.*, one in which the association is continually altering with the temperature. The gas equation would hold for the gas NO_2, and it would hold equally for the gas N_2O_4, but it will not apply throughout the range of temperature in which $N_2O_4 \rightleftarrows 2NO_2$. The gas equation might in like manner hold for the osmotic pressure of a substance in solution in water of the molecular weight 18, and it might also hold for water of the molecular weight 3×18, but water, as we know it, is neither of these compounds. It is a substance the association of which is continually changing with the temperature and the attempt is therefore being made to apply the gas equation in the range of temperature throughout which $(H_2O)_n \rightleftarrows nH_2O$.

Van Laar has, like Planck, treated the osmotic pressure of dilute

solutions from the thermodynamical standpoint and confirmed the latter's conclusion that association of the solvent does not influence the osmotic pressure. I quote here literally what Van Laar says on this matter (*Zeit. physikal. Chem.*, 1895, **18**, 274):—

"We found that the osmotic pressure $\pi = R\tau\sigma(1+a)/v_{a'}$, where $\sigma(1+a)$ has the value Σc_2*, and $v_{a'}$ the volume of one gram molecule of the pure solvent. For water $v_{a'}$ was therefore given the value 18. *If, however, association occurs, the weight of the gram molecule would be* $18a$, *so that for* $v_{a'}$ *the volume of* $18a$ *grams of water must be substituted. Calling this last* $V_{a'}$ *then* $V_{a'} = av_{a'}$. But also σ the concentration of the dissolved substance, becomes a times greater. For we have now no longer one molecule of the dissolved substance to n molecules of water (taking the mol. wt. of water = 18) but one molecule to n_1/a molecules of water, so that the concentration must be expressed by an a times greater number than before. Calling this C, then as $C = a\sigma$, the expression $\pi = R\tau C(1+a)/V_{a'}$ does not differ from $\pi = R\tau\sigma(1+a)/v_{a'}$, where the quantities $v_{a'}$ and σ are independent of the association."

The italics in the above are mine, for it is to this portion of the paragraph that I wish to direct attention more especially. The molecular volume of any compound is given by M/d, where M is the molecular weight of the compound and d its density. Now Van Laar supposes that if liquid water had the molecular weight 18, its molecular volume would be 18/1, or if it had the molecular weight $18a$, its molecular volume would be $18a/1$. In other words, the same density is to be assigned indiscriminately either to the monomolecular or to the associated compound. But can any one doubt if *liquid* water were obtainable having the molecular weight 18, that it would most certainly not have the density 1 at ordinary temperature? Take water merely as the first term of the $C_nH_{2n+1}OH$ series of alcohols, a series the members of which are themselves associated, but not to the same extent as water, and analogy at once points to a much lower density than 1 for *monomolecular* liquid water, a density that is in fact probably not far removed from $1/a$. In fact there is absolutely no evidence that the molecular volume of an associated liquid does differ greatly from that of the same liquid compound in the monomolecular state. Van Laar's argument *against* is converted therefore into an argument *for* the effect of association on the osmotic pressure.

* The c here is the n of the Planck formula.

RESEARCH FUND.

A meeting of the Research Fund Committee will be held in December. Applications for grants, accompanied by full particulars, should be sent to the Secretaries on or before December 11th.

KEKULÉ MEMORIAL LECTURE.

The Kekulé Memorial Lecture will be delivered by Professor F. R. Japp, LL.D., F.R.S., at an extra meeting of the Society on Wednesday, December 15th, at 8.30 p.m.

At the next meeting, on December 2nd, there will be a ballot for the election of Fellows and the following paper will be read.

"On Collie's space formula for benzene." By F. E. Matthews, Ph.D.

RICHARD CLAY AND SONS, LIMITED, LONDON AND BUNGAY.

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PROCEEDINGS

OF THE

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No. 185. Session 1897–8.

December 2nd, 1897. Professor Dewar, F.R.S., President, in the Chair.

Certificates were read for the first time in favour of Messrs. Charles Edward Brittain, B.Sc., 11, Highfield, Scarborough; William Arthur Caldecott, B.A., Box 1891, Johannesburg, S.A.R.; John Cooper, B.Sc., 20, Derwentwater Road, Gateshead; Frederick Cowling, Clay Cross, near Chesterfield; Wilbraham T. A. Edwards, Reduit, Mauritius; Frederick Gilderdale, 3, Havelock Street, Newcastle; William Setten Gilles, Coniston, Cedars Road, Beckenham; William Hobson Mills, B.A., Jesus College, Cambridge; Frank Forster Renwick, Glengall, Woodford Green, Essex; William Colebrook Reynolds, 64, Lydford Road, Paddington, W.; Andrew Jamieson Walker, B.A, Kilycadden, Killygordon, Co. Donegal; Ernest Charles Weismüller, 30, Pepys Road S., New Cross, S.E.

The following were duly elected Fellows of the Society:—John Ball, Ph.D.; William Ball; Alec. Alfred Beadle; Richard Oxley Burland, J.P.; Alexander McLean Cameron; Alexander Clarkson; Frank Collingridge, B.Sc.; James Murray Crofts, B.A.; John Daniell; Andrew James Dixon, F.I.C.; Oscar Guttmann, F.I.C.; Robert Hamilton; John Harger, B.Sc., Ph.D.; James Walter Horseman; Charles Kelly; Tom Lemmey, B.A.; James Scott Maclaurin, D.Sc.; Alan Macmullen, B.A.; Charles Jodrell Mansford, B.A.; Edward Masters; John A. Mathews, M.A., M.Sc.; Philip George Gregory Moon; James Charles Philip, B.Sc., Ph.D.; Alexander Ferguson Reid; Ernest Henry Roberts; Edward Sydney Simpson, B.E.; Robert Francis Wood Smith; Thomas Southern, Junr.; Frederick William Steel; Michael Edmund Stephens; George Stubbs; Edward Howard Tripp, Ph.D.; John Scriven Turner; Framjee Khurshedjee Viccajee; Percy John Vinter, M.A.; Arthur James While; Francis Samuel Young, M.A.

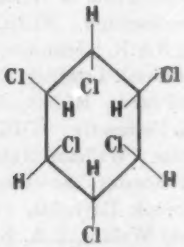
The PRESIDENT called the attention of Fellows to the fact that, although according to the Council regulations no paper could be announced which had not been received, it was open to any Fellow to make a communication at a meeting of the Society in the event of there being available time, provided that he handed a written statement to the Secretaries of the essence of his communication.

In answer to a question from Dr. HAKE, the PRESIDENT said that the appearance of such communications in the Proceedings would be subject to the editorial discretion of the Secretaries, and that when presented as full papers they would come before the Publication Committee in the usual way.

The following papers were read :—

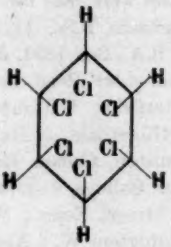
***124. "The representation of the isomeric benzene hexachlorides by Collie's space-formula." By Francis Edward Matthews, Ph.D.**

This paper discusses Collie's space-formula for benzene from the point of view of the halogen hex-addition compounds. The formula is shown to explain the existence of two isomeric hexachlorides satisfactorily, and the following formulæ are proposed for these compounds :—



α-Compound.

and



β-Compound.

These formulæ likewise explain the differences in stability towards alcoholic alkalis. The α-substance, containing the chlorine in the ortho-position to, and on the same side of the carbon nucleus as the hydrogen-atoms with which it is removed in the form of hydrogen chloride, is readily decomposed ; the β-substance, in which the hydrogen and chlorine are on opposite sides of the nucleus, has much greater stability. The remainder of the paper discusses the formation of benzene di-derivatives from mono-derivatives, and it is maintained that their formation is best explained by assuming the previous formation of unstable *ortho*-addition-compounds instead of unstable *meta*-compounds, as Collie has suggested.

DISCUSSION.

Dr. WYNNE asked whether any explanation could be given of the formation of 1 : 2 : 4-trichlorbenzene from the benzene hexachlorides by the action of alcoholic potash. The usually accepted formulæ for

benzene gave no clue to the reason for the production of unsymmetrical derivatives in such cases, and he was unable to see that the formulæ now proposed were more satisfactory in this respect.

Dr. LAPWORTH pointed out that the author's statement as to the impossibility of explaining the production of two different hexachlorides from benzene by means of any formula prior to Collie's, appeared to need qualification. It is easily seen that Kekulé's formula represents several stereoisomeric substances, as each "doubly bound" pair of carbon atoms may form a fumaroid or maleoid combination. Taking into consideration the circumstance that, for a number of reasons, the formula must be considered as a labile one, the positions of the ethylenic and single linkings being supposed to alternate, it is not impossible that, under the conditions of interaction of chlorine and benzene, the latter may react in the form of two or more of its possible stereoisomers. The addition of chlorine to a pair of carbon atoms double bound as in fumaroid compounds would, of course, afford a trans-dichloro-derivative, whilst a cis-dichloro-compound would result if the original combination were of the maleoid type. Kekulé's formula, therefore, would appear to afford a perfectly satisfactory explanation of the production of more than one benzene hexachloride.

Mr. E. J. PARRY asked if Dr. Matthews had any experimental evidence for assigning the symmetrical formula to the α-hexachloride, and the unsymmetrical to the β-compound. If the explanations of substitution offered by Collie and the author were correct, there should certainly be twice as much ortho- as para-dichlorbenzene produced when chlorbenzene is chlorinated. Further, he could not understand why, if these explanations were correct, the nitration of chlorbenzene should give ortho- and para-compounds whilst the chlorination of nitrobenzene, or the nitration of nitrobenzene, should yield meta-compounds.

Dr. MATTHEWS, in reply, stated that it had always seemed to him a remarkable fact that 1 : 2 : 4-trichlorbenzene alone was produced by the action of alkalis upon the benzene hexachlorides. He had made several attempts with large quantities of material to isolate the symmetrical modification, but always without result. The formation of the 1 : 2 : 4-compound could, however, be easily explained, either by Kekulé's or Collie's formula.

With regard to Dr. Lapworth's remarks, the formulæ proposed above account for the production of two and not of a greater number of isomerides which might be expected if these hexachlorides were regarded as cis- and trans-modifications; whilst certain properties of the compounds do not seem to harmonise with the idea that they are stereoisomerides.

The answer to Mr. Parry's questions are contained in the paper itself, the difference in stability of the two hexachlorides towards alkalis is explained by assuming that hydrogen chloride is more readily removed from atoms in the ortho-position and on the same side

of the carbon nucleus than from those in which these conditions do not obtain. Hence the above formulæ were assigned.

***125. "Compounds of piperidine with phenols." By Otto Rosenheim, Ph.D., and Philip Schidrowitz, Ph.D.**

With a view of obtaining substances of the general formula $(C_6H_{(6-n)})(C_5H_{10}\cdot N)_n$, which seemed to be of interest on account of their relation to the phenylenediamines and polyamines, the authors studied the action of piperidine on phenols and their derivatives in the presence of dehydrating agents. Although so far unsuccessful in this direction, a series of addition products in the nature of salts was observed, in which piperidine acts as the base, and the phenol as the acid. They are well crystallised compounds, easily obtained by the interaction of their components, usually in ethereal solution. They are resolved into their constituents by strong acid or alkalis. M. Oechsner de Coninck (*C. R.*, 1897, **124**, 563) describes a number of colour reactions obtained by the action of piperidine and other bases on phenols in dilute aqueous solution, but has apparently not observed the formation of the addition compounds described in the paper.

The influence of the number and position of the oxy- and nitro-groups in the phenols on the additive capacity of the piperidine molecule was studied, but no general rule could be deduced.

The following compounds were analysed, and are described in the paper: Compounds of piperidine (1 mol.) with pyrocatechol (2 mols.), guaiacol (2 mols.), hydroquinone (1 mol.), pyrogallol (1 mol.), vanillin (1 mol.), *o*- and *p*-nitrophenol (1 mol.), picric acid (1 mol.), 1 : 2 : 4-dinitronaphthol (1 mol.). Phenol, *p*-chlorphenol, resorcinol, phloroglucinol, *m*-nitrophenol, and α- and β-naphthol did not furnish crystalline compounds.

KEKULÉ MEMORIAL LECTURE.

The Kekulé Memorial Lecture will be delivered by Professor F. R. Japp, LL.D., F.R.S., at an extra meeting of the Society on Wednesday, December 15th, at 8.30 p.m.

At the next meeting, on December 16th, the following papers will be read. The authors of those marked with an asterisk have announced their intention of being present.

* "Stereochemistry of unsaturated compounds. Part I. Esterification of substituted acrylic acids." By J. J. Sudborough, Ph.D., D.Sc., and Lorenzo L. Lloyd.

* "Formation and hydrolysis of esters." By J. J. Sudborough, Ph.D., D.Sc., and Martin E. Feilmann, B.Sc.

* "A new method of determining freezing points in very dilute solution." By M. Wilderman, Ph.D.

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PROCEEDINGS

OF THE

CHEMICAL SOCIETY.

EDITED BY THE SECRETARIES.

No. 186. Session 1897–8.

December 15th, 1897. Extra Meeting. Professor Dewar, F.R.S., President, in the Chair.

Professor F. R. Japp, LL.D., F.R.S., delivered the Kekulé Memorial Lecture.

Friedrich August Kekulé was born at Darmstadt on September 7th, 1829. Originally intended for the profession of an architect, he was induced, by hearing Liebig's lectures, to devote himself to chemistry. After studying under Liebig, he spent a year in Paris, where he became intimate with Gerhardt. Later on, he resided for a time in London, making the acquaintance of Williamson and Odling. He always acknowledged the influence which these three chemists had exercised on the formation of his opinions. Kekulé's theories are based on Gerhardt's type theory; on Williamson's theory of polyvalent radicles, which, by their power of linking together other radicles, render possible the existence of multiple types; and on Odling's theory of mixed types, which was a deduction from Williamson's theory. Less consciously, perhaps, his opinions were influenced by E. Frankland's theory of the valency of elementary atoms, and by Kolbe's speculations on the constitution of organic compounds. Kekulé gathered together the various ideas which he found scattered throughout the writings of his predecessors, added to them, and welded the whole into the consistent system which forms our present theory of chemical structure. In 1857, in the course of a memoir on the constitution of fulminic acid, he gave a tabular arrangement of compounds formulated on the type of marsh gas, this being the earliest statement, although put forward only in an imperfect form, of the tetravalency

of carbon. In the same year, he published an important theoretical paper: "On the so-called Conjugated Compounds and the Theory of Polyatomic Radicles," which contains a complete system of multiple types and mixed types. In 1858, the celebrated paper, "On the Constitution and Metamorphoses of Chemical Compounds, and on the Chemical Nature of Carbon," appeared; it embodies the fully developed doctrine of the tetravalency of carbon, together with Kekulé's views on the linking of atoms and on the valency of such chains of atoms—the foundation on which our modern system of constitutional formulæ rests. In 1865, Kekulé put forward his well-known benzene theory—the crowning achievement, in his hands, of the doctrine of the linking of atoms, and the most brilliant piece of scientific prediction to be found in the whole range of organic chemistry. The conception of closed chains, or cycloids, which he thus introduced has shown itself to be capable of boundless expansion.

Kekulé published the first instalment of his *Lehrbuch der organischen Chemie* in 1859. The work was never finished; but it was instrumental in widely disseminating Kekulé's views and exercised enormous influence on the development of the science.

Kekulé obtained the *venia legendi* in Chemistry at the University of Heidelberg in 1856. Two years later he was called, as ordinary professor, to the University of Ghent, where he remained until 1867, when he was appointed to the Professorship of Chemistry in the University of Bonn, a post which he continued to hold until his death on July 13th, 1896. During his later years he suffered from bad health.

The characteristic note of Kekulé's great theoretical creation, the chemistry of structure, is the treatment of the problem of isomerism —the problem which first necessitated the use of constitutional formulæ—as one of geometrical symmetry. Kekulé's formulæ, freed from the fetters of the type theory with which he at first encumbered them, were merely more or less symmetrical geometrical figures. In order to predict the number of substitution compounds, it was only necessary to consider the degree of dissymmetry of the parent compound: the less the symmetry, the greater the number of isomeric substitution compounds. The extraordinary fertility of this conception is shown by the development which it has undergone at the hands of van't Hoff, J. Wislicenus, von Baeyer, and others.

The accuracy of Kekulé's predictions has done more to inspire a belief in the utility of legitimate hypotheses in chemistry, and has therefore done more for the deductive side of the science than that of almost any other investigator. His work stands pre-eminent as an example of the power of ideas. A benzene formula, consisting of a few chemical symbols jotted down on paper and joined together by lines, has supplied work and inspiration for scientific organic chemists

during an entire generation, and affords guidance to the most complex industry the world has yet seen.

Dr. Hugo Müller, as probably the oldest personal friend of Kekulé present, moved a cordial vote of thanks to Professor Japp for his eloquent lecture, and added his special appreciation of the admirable and exhaustive manner in which the lecturer had accomplished his task. A considerable effort was needed to realise the condition in which organic chemistry stood fifty years ago, in order to recognise the vast advances which have been made in the interval. It may be truly claimed for Kekulé that he holds a foremost position amongst those reformers who have initiated this progress. It was here, in London, that Kekulé first conceived the ideas which, in their further development, assumed the shape of his "chemistry of carbon" and "benzene theory," and being in those days in almost daily intercourse with him, he well recollected the eagerness and enthusiasm with which the problems which occupied his mind were discussed.

Soon afterwards, in Heidelberg, and then in Ghent, his affable manner and sociability attracted a number of devoted pupils, who became active fellow-workers, and thus his teaching bore fruit in all directions.

Unfortunately, not long after he had been settled in Bonn, his health gradually gave way, and he suffered much from nervous prostration and an irksome degree of deafness, which at times much depressed him. His power of work became greatly impaired, and notwithstanding repeated heroic efforts, even his Handbook had to remain unfinished.

Professor Thorpe, in seconding the resolution, also desired to give expression to the sense of obligation which the Society was under to Professor Japp for the thoughtful and eminently impartial address which he had given. There was, however, one slight but characteristic omission in the lecture. In enumerating Kekulé's students, Dr. Japp had neglected to make any reference to himself. It was, no doubt, that same feeling of piety to which he had borne witness in the course of his lecture on the part of another which induced Dr. Japp to comply so readily as he had done with the request of the Council that he should undertake the weighty and responsible duty of delivering this address. His personal intercourse, as a student, with the master had, we may take it, quickened his appreciation of his work. At the same time, as would be evident, it had in no sense diminished his critical faculty. The audience had recognised that the lecture was a truthful and well-balanced account, written impartially and in the true spirit of history, of the origin and fruit, so far as this had been gathered, of the great chemist's labours.

Some reference had been made to the fact that he (the speaker) had enjoyed the good fortune of also being a student under Kekulé, and of being associated with him, in some small degree, in certain experimental work which he undertook during the first years of his professorship in the magnificent institution which Germany owes to Hofmann. It is a curious coincidence that Hofmann, like Kekulé, might have become an architect, if destiny, as in Kekulé's case, had not intended that he should be a chemist. During the late sixties there was no sign of the decay in intellectual vigour which a few years later became so sadly obvious. At that time, the great generalisation which we associate with Kekulé's name was still, to some extent, on its trial, and it had to withstand the assaults which were from time to time delivered by keen and active opponents in other schools of chemical thought. It happened that very shortly after the speaker's entrance into Kekulé's laboratory, he was called upon to handle the weapons which Kekulé himself placed in his hands in order to defend a small, but apparently vulnerable point, in the theory. That circumstance proved of incalculable benefit to him, in that it brought him into intimate personal contact with Kekulé, and enabled him to see something of his methods of work, and of the springs of his intellectual activity. Dr. Japp has ably testified to Kekulé's merits as a teacher. Kekulé, indeed, was one of the very best expositors, with the single possible exception of Kirchhoff, to whom it had been the speaker's lot to listen. As a laboratory teacher he was excellent. He was a most severe judge of work, striving to exact the same high manipulative finish, the same neatness and order, which he invariably bestowed on everything he did, and he was absolutely intolerant of anything slovenly or 'sloppy.' But it was as a lecturer that he was seen at his best. He was singularly luminous as a thinker, a close and accurate reasoner, with a remarkable power of concentrated expression. He was not a rapid speaker, and he never indulged in those rhetorical flights with which Hofmann occasionally was wont to electrify an audience. His language was apt and well chosen, and his delivery easy and natural. His lecture-table was never overburdened with 'experiments'; those he showed were strictly proper to the subject in hand. To see him handle the chalk was in itself a liberal education. Although everything appeared to be so easy and natural, an attentive critic could hardly fail to perceive that the lecture had been carefully thought out beforehand, possibly over a longer period of time than it took to utter. Every detail would seem to have been considered, even to the particular places on the black-board where the formulæ should appear.

During the later period of his life, Kekulé, unfortunately for Science, was comparatively sterile. Those who knew him, however, would be the first to affirm that this seeming apathy sprung from no natural

indolence. There is no doubt that he suffered, even in the early period of middle life, from the intense stress and strain of his mental labours prior to the Ghent period. He had too surely exemplified the sad truth of Liebig's saying, to which Dr. Japp had referred, that he who would become a great chemist must pay for his preeminence by the sacrifice of his health. There is reason to know that it was the consciousness of failing power which prevented him from finishing much to which he had put his hand, and that his fastidiousness and his sense of "finish," amounting almost to hypercriticism, restrained him from publishing what he realised fell short of his ideal. What he has left us, however, is an imperishable monument to his genius.

The PRESIDENT said that there was little to add to Professor Japp's exhaustive eulogy of the life and work of Kekulé. His own early relations, however, with the great chemist whose life work the Society was commemorating might have some interest to the members and ought to be told. While a student with Lord Playfair at Edinburgh, in the session 1866—67, he made his first contribution to Science in the shape of a little paper entitled, "On the Oxidation of Phenyl Alcohol and a Mechanical Arrangement adapted to Illustrate Structure in the Non-saturated Hydrocarbons." This note appeared in the *Proceedings of the Royal Society of Edinburgh*, and he was so desirous of becoming known to Kekulé as a student of his theory of the aromatic bodies that a specimen model was sent to Ghent. Lord Playfair addressed a letter to Kekulé stating that he (Professor Dewar) was very anxious to work in his laboratory. The reply was "Come," and the reception and kindness he received from Kekulé has always had his profound gratitude.

The summer of 1867 was thus spent in the private laboratory of Kekulé. Before leaving Edinburgh, he had been working on the coal tar bases, and a supply was taken with him to Ghent. There he began the study of the oxidation products of picoline, and at the British Association Meeting at Norwich, in 1868, an account of the separation of dicarbopyridinic acid, the analogue of phthalic acid in the benzene series, was given. At the same meeting, he gave a paper on "Kekulé's Model to Illustrate Graphic Formulæ." This is the succinct history of the beginning of the pyridine-benzene analogy. His old friend, Koerner, had speculated in the same direction, and he (Prof. Dewar) might confess that in his opinion they both had received too much credit for an extension of the benzene theory to pyridine. At a distance of thirty years, to look back and call to mind the presence and personality of the great chemist as he knew him was indeed a pleasure. He was a man of noble mien, handsome, dignified, and yet of a homely and kindly disposition. He was a severe critic, having a haughty contempt for the

accidental and *bizarre* in scientific work. His originality and suggestiveness seemed endless, so that he had no need to commit scientific trespass or to follow just in the wake of other people's ideas. Everything that passed through the Kekulé alembic was indeed transmuted into pure gold. His precision of thought and diction rendered his papers profoundly suggestive to other workers. His great work will always live in the history of our Science, and his loving memory will be for ever enshrined in the hearts of his pupils.

December 16th, 1897. Professor Dewar, F.R.S., President, in the Chair.

Messrs. James C. Philip, Edward Rosling and Frank T. Addyman were formally admitted Fellows of the Society.

The PRESIDENT announced that the following had been recommended by Council for election as Foreign Members, to be balloted for at the next meeting, January 20th, 1898.

Prof. Remsen, Baltimore, U.S.A.; Prof. Troost, Paris; Prof. Moissan, Paris; Prof. Raoult, Grenoble; Prof. Ostwald, Leipzig; Prof. Curtius, Bonn; Prof. Mensutkin, St. Petersburg; Prof. Markownikow, St. Petersburg; Prof. Arrhenius, Stockholm; Prof. Waage, Christiania; Prof. Franchimont, Leyden; Prof. van der Waals, Amsterdam; Prof. Spring, Liége; Prof. Körner, Milan.

Certificates were read for the first time in favour of Messrs E. L. Allhusen, B.Sc., Geological Survey, Perth, W.A.; B. S. Bull, M.A., B.Sc., Ph.D., 49 Devonshire Road, Greenwich; T. H. Hills, 6 Eliot Park, Blackheath; J. E. Miller, Holmoor, Patrington, Hull; G. T. Morgan, 35A Russell Road, Kensington, W.; W. E. Moss, B.A., Burnthwaite, Bolton; H. Poole, 323, W. 34th Street, New York; W. Richards, Old Elvet, Durham.

The following papers were read :—

***126. "Stereochemistry of unsaturated compounds. Part I. Esterification of substituted acrylic acids." By John J. Sudborough and Lorenzo L. Lloyd.**

In order to determine whether there is any general rule applying to the esterification of unsaturated acids, similar to those discovered by Mensutkin for fatty acids, and by Victor Meyer and Sudborough for aromatic acids, the authors have investigated the following acids: cinnamic acid, allocinnamic acid, atropic acid, ortho-, meta-, and para-nitrocinnamic acids, α-bromocinnamic acid, α-bromallocinnamic acid, two β-bromocinnamic acids, two α-β-dibromocinnamic acids, α-β-dichlorcinnamic acid, α-β-di-iodocinnamic acid, α-cyanocinnamic acid, α-cyano-meta- and α-cyano-ortho-nitrocinnamic acid, α-phenylcinnamic

acid, α-phenylallocinnamic acid, six α-phenylnitrocinnamic acids, triphenylacrylic acid, α-β-di-iodoacrylic acid. Half a gram of each acid was boiled for an hour with 10 c.c. of a 3 per cent. solution of hydrogen chloride in methylic alcohol, and the amount of ester formed determined in the usual manner.

The authors draw the following conclusions from the results which they have obtained :—

(1) Unsaturated acids of the types,

$$H(Y)C{:}C(X)CO_2H \quad \text{and} \quad Z(Y)C{:}C(X)CO_2H,$$

yield but small amounts of ester when treated in the manner described.

This furnishes a ready method for distinguishing stereoisomeric acids. (1) $H(Y)C{:}C(X)CO_2H$ and (2) $H(Y)C{:}C(CO_2H)X$.

As acids of the trans- type (1)are esterified with difficulty, and acids of the cis- type (2) with ease by the above method, it is probable that the method can also be used for separating mixtures of such acids, in very much the same manner that diortho-substituted benzoic acids can be separated from their isomers.

(2) An α-substituted acrylic acid, $CO_2HC(X){:}CH_2$, is more difficult to esterify than a β-substituted acid, $CO_2HC(H){:}CHX$.

(3) In certain substituted cinnamic acids, a nitro-group in the ortho-position appears to have a retarding influence. The results obtained are completely in accord with those published by Anschütz (*Ber.*, 1897, 30, 2652) whilst the present work was still being carried out.

The constitution of camphoric acid is discussed in the light of the results contained in the paper.

The authors think it desirable to carry out similar researches with substituted acids ; they have already found that dibromosuccinic acid, phenyldibromopropionic acid and its nitro-derivatives, yield but little ester when boiled for an hour with a 3 per cent. solution of hydrogen chloride in methylic alcohol. Several new methylic esters have been obtained, and are described in the paper.

***127. "Formation and hydrolysis of esters." By John J. Sudborough, Ph.D., D.Sc., and Martin E. Feilmann, B Sc.**

From the researches of Mensutkin (*Annalen*, 1879, 195, 334, 1879, 197, 193) on the esterification of fatty acids, of Victor Meyer and Sudborough (*Ber.*, 1894, 27, 510, 1580, 3146) on substituted benzoic acids, and of Sudborough and Lloyd (preceding abstract) and Anschütz (*Ber.*, 1897, 30, 2652) on unsaturated acids, the authors consider it proved beyond doubt that stereochemical influences play a most important part in the esterification of an acid by means of an alcohol and hydrogen chloride. Researches by Kellas (*Z. physik. Chem.*, 1897,

25, 221) on the esterification of monosubstituted benzoic acids, and of Sell (Trans., 1897, 71, 1070) on substituted pyridinecarboxylic acids also support the same conclusion. In the benzoic and acrylic acid series, the chemical nature of the substituting groups has but little, if any, influence on the retardation of esterification. CH_3, F, Cl, Br, I, NO_2, OH and CO_2H groups all act in the same manner; the radicle weight or volume, however, affects the retardation to a certain extent (Meyer, *Ber.*, 1895, 28, 1259, and Kellas, *loc. cit.*).

One would therefore conclude that in the fatty series, too, the chemical nature of the substituting groups would have but little, if any, apparent influence. A tertiary fatty acid, however, such as trimethylacetic acid, yields but little ester when heated with alcohol (Mensutkin), whilst the similarly constituted trichloracetic acid is most readily esterified, in fact, much more readily than acetic, mono- or di-chloracetic acids (Lichty, *Am. Chem. J.*, 1896, 18, 590). This difference in behaviour we can only attribute to the enormous increase in strength of the acid.

	K		K
(1) Acetic acid	0·0018	(3) Dichloracetic acid	5·14
(2) Chloracetic acid	0·155	(4) Trichloracetic acid	121·0

Lichty's researches show that these four acids follow exactly the order given above as regards the ease with which they are esterified. The amounts of ester formed at the end of any given time by no means bear the same ratio to one another as do the affinity constants of the corresponding acids.

	After 1 min.	1 hour.	2 hours.
Chloracetic	1·78	41·89	57·33 per cent.
Dichloracetic ...	4·56	56·49	62·34 „
Trichloracetic ...	9·99	59·39	66·18 „

It would appear then that some other factor is introduced which tends to hinder the formation of the esters, and this factor the authors consider to be the stereochemical influence of the chlorine atoms. The general conclusion drawn is that in the conversion of an acid into its ester by the action of an alcohol, either with or without hydrogen chloride, the rate of esterification is determined by two factors:—1. The configuration of the acid, in other words, the presence of substituting groups situated close to the carboxylic group, which always tend to hinder esterification. 2. The strength of the acid as determined by its affinity constant. In most of the cases which have been more closely studied, the first factor is the more prominent, and obscures, to a large extent, the influence of the second factor. In exceptional cases, however, namely, in acids the strength of which has been enormously increased, the second factor becomes the more prominent, and the influence of con-

figuration is cloaked. In all cases, however, we must suppose the two factors to be in force, and it is only in acids which have the same affinity constant that the true effect of stereochemical influence can be looked for.

No general systematic study of the rate of hydrolysis of esters appears to have been attempted. Victor Meyer (*Ber.*, 1895, **28**, 1263) formulated the generalisation that those esters which are the most difficult to form are also the most difficult to hydrolyse. This view was also held by Wegscheider (*Ber.*, 1895, **28**, 2536) and Brühl, but according to the more recent investigations of Kellas, this generalisation is not strictly correct. Kellas (*loc. cit.*) studied the rate of hydrolysis of the methyl salts of monosubstituted benzoic acids by means of alkali. He found that in any given series the ortho-compound is always the most difficult to hydrolyse, the para- occupies an intermediate position, and the meta- is most readily hydrolysed (with the exception of the nitro-compounds). It is stated, however, that methylic orthonitrobenzoate is much more readily hydrolysed than methylic orthotoluate, although the nitro-ester is formed much more slowly than the toluate. This and similar results noted by Kellas, for example, the fact that methylic benzoate is difficult to hydrolyse, can be accounted for by the introduction of the affinity of the acid as a factor. For orthonitrobenzoic acid $K = 0{\cdot}616$, for orthotoluic acid $K = 0{\cdot}012$, and for benzoic acid $K = 0{\cdot}006$. The results obtained by Hjelt (*Ber.*, 1896, **29**, 1864) on the hydrolysis of the ethylic salt of substituted malonic acids also lead to the same conclusion. They indicate that here, also, the rate of hydrolysis does not depend merely on the stereochemistry of the ester molecule. If the affinity constants are taken into consideration, the obstruction due to the substituting groups is much more pronounced (with the exception of ethylic allylmalonate). Investigations by the authors on the hydrolysis of the ethylic salts of acetic, methyl-, dimethyl-, and trimethylacetic acids by the aid of sodium hydroxide, prove that here, where the affinity constants of the acids vary but little—acetic acid $K = 0{\cdot}0018$; propionic acid $K = 0{\cdot}00134$; isobutyric acid $= 0{\cdot}00144$, and trimethylic acetic acid (unknown, but at any rate very small, since the salts of this acid are extremely unstable),—the rates of hydrolysis are what would be expected from the introduction of the substituting groups—

Hours.	0·25	0·5	1	1·5	2·5	3	4	4½	8	10	22·5	70	
Ethylic acetate.....	19·6	28	42			66			82·6	85·4			per cent.
,, propionate.....	14·4	19·6		35·6		50·8		61·2					,, ,,
,, isobutyrate.....	5·2	7·2	11·4		19·2						61		,, ,,
,, trimethylacetate				2·4			6·8		8·6			19·6	,, ,,

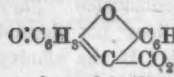
With the esters of chlorinated and brominated acetic acids, the reverse is true, and all are decomposed much more readily than ethylic acetate

itself. Comparative experiments with these esters are being undertaken by the authors.

The general conclusion arrived at is, therefore, that in the hydrolysis of esters by the aid of an alkali, the same two factors operate as in esterification. The strength of the acid which is formed by the hydrolysis of the ester seems, however, to play a more important part than it did in esterification, and this accounts for the fact that it does not always follow that esters which are most readily formed are the most readily hydrolysed.

Other factors are apparently introduced when esters are hydrolysed by the aid of hydrochloric acid, as it has been proved that esters by no means arrange themselves in the same order when hydrolysed by an alkali as when hydrolysed by an acid (Hemptinne, *Z. physik. Chem.*, 1894, **13**, 561; Löwenherz, *ibid.*, 1894, **15**, 389; Van Dyken, *Rec. Trav. Chim.*, 1895, **14**, 106). The authors consider that these generalisations can be proved or refuted only by a much more careful study of the hydrolysis of numerous series of esters. They themselves intend investigating the ethylic salts of substituted (alkylated) succinic acids, as the strengths of these acids differ but little, and therefore the results obtained should throw light upon the retarding effect of different alkylic groups.

Discussion.

Dr. Hewitt said that the fact that hydroxylfluoronecarboxylic acid,  , yields scarcely any ethyl ester, even after prolonged boiling with 9 parts by weight of ethyl alcohol and 1 part of concentrated sulphuric acid, is easily explicable in the light of Dr. Sudborough's work. Hydroxylfluoronecarboxylic acid is a trisubstituted acrylic acid, and hence should not easily esterify. On the other hand, Victor Meyer showed that triphenylacrylic acid, $Ph_2C{:}C(Ph){\cdot}CO_2H$, yielded an ester by prolonged boiling with methyl alcohol and a stream of hydrogen chloride. Under similar circumstances, triphenylacetic acid, $(C_6H_5)_3CO_2H$, furnished very little ester.

Dr. Shields called attention to the numbers, quoted by the authors of the papers, representing the percentage amount of etherification after one minute, one hour, and two hours, and remarked that, whereas all the limiting values were approximately the same after sufficient time had elapsed, a considerable difference existed between the numbers when the amount of transformation was measured after the lapse of only one minute. If it had been possible to obtain the corresponding values after one second, he thought the difference would have been

still greater, and that in any serious attempt to study parallelism between the velocity of etherification and the affinity constants of the acids, it would be necessary to determine the velocity constant of the reaction or the initial rate of etherification.

*128. "A new method of determining freezing points in very dilute solution." By Meyer Wilderman, Ph.D.

The chief condition for obtaining correct determinations of the freezing point is the establishment of equilibrium between the solid and the liquid part of the heterogeneous system. Starting from the properties of "perfect" equilibrium, and from the equations for velocity of ice-melting, ice-separation, and Newton's equation for cooling, all the conditions necessary for a successful experiment, previously laid down empirically by the late P. B. Lewis and then by the author, are now deduced from theoretical considerations. It is shown how to arrange the equilibrium with an accuracy of 0·00002—0·00006° and even greater. The freezing point method, which has been hitherto a conglomeration of empirical rules, is thus placed on a physico-mathematical basis, and the experimental error of all previous methods can be calculated. The second important point in a freezing point method is a correct and very detailed knowledge of the registering instrument. A very careful study of the errors of mercury thermometers has been made for a long time, and an account of this is given. This paper is a continuation of that by P. B. Lewis (Trans., 1895, 67, 1).

Discussion.

Mr. Pickering expressed his disappointment that the author had not made any statement as to what his "new method" was. All that he had given was a summary, in the form of an equation, of the various inaccuracies inherent in freezing point determinations generally. These inaccuracies were well-known, and it was of great importance that they should be reduced to a minimum; but it was impossible to say whether the author's new method succeeded in doing this or not until a description of the method was given.

Dr. Shields remarked that the literature and controversies on the vexed question of the accurate determination of the freezing point of dilute solutions would already fill a large volume. Since the subject was one of great importance in connection with the modern theory of solutions, any new contribution which was likely to lead to a final settlement of the conflicting views was welcome. He regretted that want of time had prevented Dr. Wilderman from giving a fuller account of his paper, but the method of attack adopted by the author

was undoubtedly a step in the right direction, and he thought that the study of the time reaction and of equilibrium in freezing solutions would lead, if it had not already in Dr. Wilderman's hands, led, to important advances.

Dr. WILDERMAN, in reply, stated that methods were given in the paper for obtaining the separated ice in fine films throughout the liquid. In answer to Mr. Pickering, he said that the value of the equations he laid down was that by them the errors due to equilibrium in the methods of other investigators could be estimated, and their results recalculated. As an illustration, one of the most accurate of the recent methods was recalculated, and its error found to be 160 times greater than his own. He had presented, for the first time, the physico-mathematical theory of freezing point determinations in such a form that future experimenters could arrange with ease the equilibrium to any degree of accuracy required.

***129. "A possible basis of generalisation of isomeric changes in organic compounds." By Arthur Lapworth, D.Sc.**

In this paper, the author points out that many isomeric changes, hitherto regarded as belonging to different types, may be formulated as special cases of a general form, which may be expressed by the reversible equation $R_\alpha M{\cdot}R_\beta{:}R_\gamma \rightleftarrows R_\alpha{:}R_\beta{\cdot}R_\gamma M$, representing a labile group moving from an α-atom to a γ-atom, the necessary rearrangement of single and double bindings taking place between the three atoms R_α, R_β and R_γ. A conventional "mechanical" representation of the change is given for the special case where R_α, R_β and R_γ are carbon atoms.

Examples, for the most part derived from "tautomeric" and "desmotropic" substances, such as acetoacetic ether, cyanic acid, nitroso-compounds, &c., are shown to be of the above type.

Extensions of the above special form are deduced, and the general conclusion is arrived at, that in a chain of alternately singly and doubly-linked atoms, either (1) a labile group may become successively attached to alternate atoms, or (2) an exchange of labile groups in γ- (*i.e.*, meta) positions may occur. These deductions are shown to be confirmed by the behaviour of benzenoid compounds, &c., the fully justifiable assumption being made that benzenoid compounds may act as if possessing Kekulé's formula. Special reference is made to nitrophenol, orthohydroxyazobenzene, the sulphonic derivatives of aniline and of β-naphthol, and also to the changes of methylaniline into paratoluidine and of hydrazobenzene into benzidine, which are all shown to exhibit changes in complete accordance with the author's views.

Further modification of the general formula for the case where R_β and R_γ are singly, instead of doubly, linked, is shown to lead to the form $R_\alpha M \cdot R_\beta \cdot R_\gamma \gtrless R_\alpha \cdot R_\beta + R_\gamma \cdot M$, which represents on the one hand the great majority of simple molecular decompositions of organic compounds, and on the other the formation of the ordinary addition products from unsaturated substances. The production of substitution derivatives, &c., by successive addition and isomeric change (compare Armstrong, Trans., 1887, 51, 258), as well as some simple cases of hydrolysis, are then discussed.

From the last formula, the following type is shown to be at once derivable: $R_\alpha \cdot M + R_\beta \cdot R_\gamma \gtrless R_\alpha \cdot R_\beta + R_\gamma M$, which represents the ordinary process of substitution in saturated compounds [compare Armstrong, *loc. cit.*, and Williamson ("Theory of Etherification," 1851)].

With the help of the foregoing principles, the author shows that the production of meta-di-derivatives from certain mono-derivatives of benzene may be consistently explained on the basis of Armstrong's suggestion (*loc. cit.*) that in such mono-derivatives addition of the acting agent to the side group precedes substitution. Further, this assumption at once explains the replacement (by a substituting group) of side groups, which otherwise afford meta-derivatives.

Some apparent exceptions to the foregoing principle are next dealt with, and it is shown that little difficulty exists in relegating to the above type the production of, for example, pinacolines from pinacones, acetanilide from acetophenone-oxime, benzilic acid from benzil, &c., on suppositions which, for the most part, the author has not been the first to make, and which mostly involve the intermediate production of ring-compounds.

It is further shown that the following type of change is possibly, but by no means necessarily, independent of the above, viz., $R_\alpha M \cdot \underline{R}_\beta \gtrless R_\alpha \cdot R_\beta M$ (where $\underline{R}_\beta$ represents an atom possessing a "residual affinity" of two units), and a possible method of harmonising this with the other type is discussed in detail.

Finally, it is pointed out that, although a brief dissociation between the labile group and its attached atom must be assumed in order to account for the above changes, cases involving electrolytic dissociation or partial destruction of the labile substance necessarily involve probable changes other than an $\alpha\gamma$-isomeric change, and should therefore be as far as possible avoided in investigating the applicability of the foregoing generalisation.

Discussion.

Dr. Wynne regretted that the author, in reading his paper, had thought it more important to enumerate the various well-known

cases of tautomerism, than to give the explanation he had devised to account for this property. So far as could be gathered, the author sought to connect those reactions in which a single radicle is transferred from one to the other of positions relatively 1 : 3 accompanied by a change of structure in the chain, with those in which mutual exchange of radicles in positions relatively 1 : 3 is brought about without any structural rearrangement. It was difficult to see wherein the analogy lay, but even if the author's contention were adopted, it was open to question whether anything had been thereby gained. The usual statement that ortho-, or para-, or both di-derivatives result from compounds of the phenylsulphamic acid type expressed the facts at least as clearly as the author's emendation, wherein the reaction is represented as being brought about by the radicle moving from any given position to the next but one. What was to be desired was an explanation of the cause of the mutual transference, not a re-statement of the fact of its occurrence.

The author's view of the formation of metanitrobenzene-sulphonic acid surely needed more explanation than the reaction for which it was put forward to account, and the same might be said of the arguments brought forward to explain the production of metasulphonic acids from aniline derivatives. A striking case of the production of such acids is exhibited by dimethylaniline, which with ordinary sulphuric acid gives the para-, whilst with fuming sulphuric acid, a mixture of the meta- and para-sulphonic acids is obtained. Yet, according to the author's views, the meta-sulphonic acid should be the sole product in either case, since he considers that compounds of the phenylsulphamic acid type—which dimethylaniline cannot form—give rise to parasulphonic, and compounds of the aniline hydrogen sulphate type—which dimethylaniline can form—give rise to metasulphonic acids.

Again, the order in which isomeric sulphonic acids seem to be formed in the case of β-naphthol had been adduced by the author in support of his views, but it was not difficult to quote cases in which it appeared to be inapplicable. Erdmann had shown that 1 : 4-, 1 : 4'-, and 1 : 3'-α-naphthylaminesulphonic acids are the products of the sulphonation of α-naphthylamine, and it was not easy to see how the production of the last named and most stable of these acids could be accounted for by the author, even if his views did not beg the question of the mode in which isomeric sulphonic acids are formed, as reference to Erdmann's paper would show.

He was, moreover, unable to follow the author in tracing an analogy between the changes involving the production of ethylene from ethyl bromide, and of ethyl bromide from ethylene on the one hand, and those occurring in tautomeric compounds on the other; an analogy, that is, between reactions involving scission of the chain, and those in

which none occurs. Markownikow's rule embraced what is known of such reactions, and the author's re-statement of some of the facts did not seem to add to, or explain, that well known summary.

Professor COLLIE said that this generalisation of Dr. Lapworth's appeared to him to be one of great importance. Any simple rule that would explain not only all cases of isomeric change amongst paraffinoid as well as amongst benzenoid derivatives, but also the hydrolysis of esters, the decomposition of diazo-compounds, the formation of meta-derivatives, &c., &c., was one which certainly claimed the attention of chemists. Moreover, it received much support from a stereochemical point of view; and if Dr. Lapworth's first equation be allowed, then the rest of the argument was a clearly worked out, logical deduction.

Dr. KIPPING agreed with the last speaker, that the paper under discussion was one of great interest and importance. Starting from a simple case of tautomeric change, by an ingenious and logical application of views already widely accepted, Dr. Lapworth had attempted to account for, and to bring into line, a very large number of cases of isomeric change, which before seemed to be complex, obscure, and not related to one another in any way. If this generalisation were possible, as it certainly seemed to be from the formulæ and explanations which Dr. Lapworth had advanced, his paper deserved, and would no doubt receive, the careful consideration of chemists.

Mr. A. G. BLOXAM asked whether, in the event of such tautomerism as that referred to by Dr. Lapworth occurring in di-substitution products, the second group would exert any preventive action on the wandering of the first group. Thus, supposing that a sulphonic group tended to wander into the next following γ-position, which, however, was already occupied by another group, would such a state of affairs determine the non-existence of a tautomeric form?

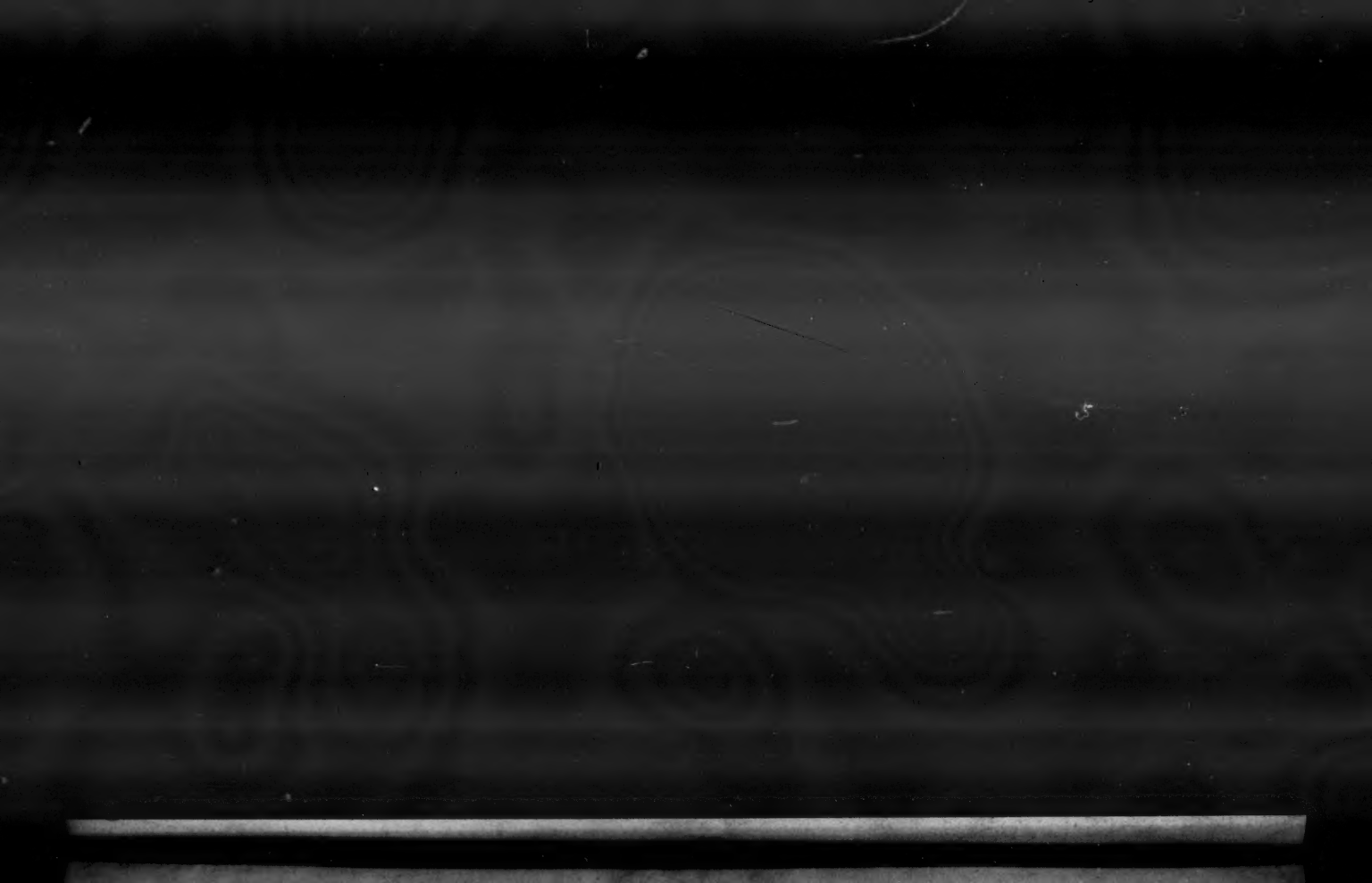
Dr. LAPWORTH, in replying, regretted that the time at his disposal had prevented him from saying all he had wished. He had tried, in the first instance, to show that a great many isomeric changes, including those of elimination of two groups attached to contiguous carbon atoms and also of most changes in benzenoid compounds, might be written in a form derived from that representing the relationship between the two forms of simple tautomeric substances, and had shown in the paper that they might be represented on exactly similar stereochemical bases. The latter he had omitted to give in reading, as it involved the introduction of the usual hypothetical space-relationships of carbon atoms and the idea of dissociation as distinct from decomposition, whilst the paper intended to call attention to what appeared to be a general type of change, logically deducible from a well-known form.

With regard to the production of benzenoid substitution-derivatives,

he had already pointed out that, as a rule, where substitution in the benzene nucleus undoubtedly occurs, ortho- and para-derivatives are the chief products, and that this fact, as also the question of the stability of a particular benzene derivative, must depend on some principle not intimately connected with the mechanism of isomeric change. A change, analogous to that of compounds of the aniline hydrogen sulphate type would afford meta-derivatives, and evidence of this is afforded by the production of metanitraniline when aniline nitrate is treated with cold sulphuric acid; the production of ortho- and para-derivatives may then be due either to direct substitution in the ring, or to isomeric change of compounds of the phenylsulphamic acid or methylaniline type. Hence the formation of any particular acid from aniline, dimethylaniline, α- and β-naphthylamines, &c., is not difficult to account for, although the exact details of the production, or any one of them, would require a special discussion.

The convenience of employing the above formulæ and the apparently very general applicability of the type of change to which the author desired to draw attention, would only be understood when it was applied to cases which, as the author shows in his paper, are difficult to discuss on the usual bases.

In reply to Mr. Bloxam, the author said that the paper dealt with cases in which the γ-position was already occupied, and in the special case alluded to, the author's view made it clear that no entirely preventive action would be exercised, and this would appear to be in accordance with known cases.

At the next meeting, January 20th, 1898, there will be a ballot for the election of Foreign Members.

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